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XXIII.—ON THE BUTANES AND OCTANES IN AMERICAN PETROLEUM.[1]

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As one of us (C. F. M.) has shown,[2] the form of the butanes and octanes in American petroleum is not so well understood as that of other constituents of the series C_nH_{2n+2}. Concerning the butanes, except that an analysis of a gas condensed at 0° by Ronalds gave the composition required for butane, very little has been published beyond the fact that distillates have been collected at 0° and at 8°–9°. It, therefore, seemed advisable to devote some time to the separation of the butanes for the purpose of ascertaining with greater precision what hydrocarbons with these boiling-points are actually contained in petroleum.

The Butanes.

The early investigations of Pelouze and Cahours[3] indicated the presence of butane in their most volatile distillates. A

[1] Presented to the American Academy of Arts and Sciences, October, 1896. Aid in the work described in this paper was given by the Academy from the C. M. Warren fund for original research.

For efficient aid in the work of this paper, I should acknowledge my obligations to Mr. W. H. Whitfield, who selected portions of the work on the butanes as the subject of a thesis for a degree of Bachelor of Science, and to my assistants, Messrs. C. A. Soch and E. Davidson.—C. F. M.

[2] Proc. Am. Acad., 31, 23.

[3] Compt. rend., 1862, p. 1241.

portion collected between 5° and 10° gave with chlorine a "chlorbutyl," boiling-point 65°–70°. In a higher distillate, whose boiling-point was not given, amyl hydride was suspected by the formation of a "chloramyl" boiling at 98°–103°, but this hydrocarbon was not further identified. In the first analysis of the gas from Pennsylvania petroleum, Ronalds[1] condensed an oil at 0°–1°, specific gravity 0.6000 at 0°, that gave the composition required for butane. Ronalds also collected an oil between 6° and 8°, specific gravity 0.6004, vapor density 2.178, which he regarded as a mixture of butane with higher constituents. As will be shown in this paper, nothing further has been done toward verifying the pentane from which the pentyl chloride of Pelouze and Cahours was obtained, although it was really derived from the pentane boiling at 30°, as we have ascertained after many trials.

Probably on account of difficulty in procuring an adequate supply of materials, Warren[2] gave less attention to the butanes than to the higher constituents. He collected a distillate at 0°, which, on the basis of Ronald's determination, he assumed was a butane. After repeated and careful distillation through his regulated condenser, Warren also separated a liquid, boiling-point 8°–9°. Although nothing further was done towards determining its composition, Warren believed this body "to have been sufficiently purified to justify the conclusion supported by analogy that there is a constituent boiling at about 8°–9°." Since no other attempts have been made to identify the butanes, further study of these bodies was evidently necessary.

In returning to this subject, we assumed at first that it would only be necessary to enforce the results already obtained, which seemed to be supported by our first determinations.[3] But as the work progressed, it soon became evident that this assumption would not be justified. Taking advantage of the extremely cold weather in January, 1895, through the kindness of Messrs. Schofield, Shirmer, and Teagle, we procured 45 liters of a second distillate of the naphtha from Pennsylvania and Ohio petroleum, the most volatile portion

[1] J. Chem. Soc., 1865, p. 54. [2] Proc. Am. Acad., **27**, 56.
[3] *Ibid*, **31**, 23.

that could be condensed with the atmospheric temperature below 0° F. Since the naphthas from Pennsylvania and Ohio petroleum are redistilled together, it is difficult to procure this portion from either crude oil unless, indeed, a run of the crude oil were made in the refinery with this object in view. But this did not seem necessary, since there can be little doubt that the constituents of the most volatile portion of Ohio and Pennsylvania petroleums are identical. During the continued cold weather of January, February, and March of the same year, distillation of this product was continued through a Warren condenser, filled with a freezing-mixture, and the temperature of the distillates was kept very low to avoid loss so far as possible. In this manner a long series of distillations was carried on with small loss, aside from transference, except of the most volatile distillates. In these volatile portions, —20° to —10°, the distillation proceeded from the heat of the surrounding atmosphere, and it was regulated by cooling the still. The results obtained in the study of these distillates were so unexpected, that the entire process of distillation was repeated several times during the colder months of the present year until in all 250 liters of 88°- and 92°- gasoline have been distilled, the portions below 12°, twenty times. The interesting results in the distillations of the present year, especially in excluding a butane at 8°–9°, are due to the patience and care of Mr. Whitfield.

In studying the derivatives of these hydrocarbons, the chlorine substitution-products were first formed by bringing together chlorine and the vapor of the hydrocarbon. The method we employed differed somewhat in details from the method of Schorlemmer.[1] In the reaction between chlorine and the hydrocarbon, the intensity of light must be carefully regulated. In direct sunlight so much heat is developed that a flame appears with the separation of carbon. On a cloudy day the action proceeds slowly, and with less light it is suspended. We obtained the most satisfactory results both as regards the progress of the reaction and the yield of the monochlorine derivative in clear sunshine with a sheet of newspaper interposed. In all our distillates the action of chlorine has

[1] Phil. Trans., 162, 111 (1872).

proceeded with great readiness in the cold. The distillates collected below 0° were well cooled by means of a freezing-mixture. The condensation of the chlorinated product was more complete in a capacious bottle,—a 2-liter bottle for 100–200 cc. of the oil, with the delivery tube extending half way from the top of the bottle to the surface of the liquid. The heavier chlorine comes into intimate contact with the vapor of the oil, and the product condenses for the most part on the side of the bottle. Some of it unavoidably escapes with the hydrochloric acid, and it may be condensed in part by placing in front another bottle well cooled, or, still better, by passing the escaping gas into water. We have not found it essential to separate by distillation the chlorinated product from the hydrocarbon until the action was finished. If it be stopped with a small amount of the hydrocarbon unchanged, which may easily be determined by experience, the product is nearly all the monochlorine compound. The use of iodine suggested by Schorlemmer has not seemed essential, at least in the formation of the butane derivatives, since, without it, there is no difficulty in obtaining 80 per cent. of the monochlorine compound, the remainder consisting for the most part of unchanged hydrocarbon, nor in our experience is the yield increased by the use of iodine. In the separation by fractional distillation of the products of the chlorination, our experience is not in accordance with that of Schorlemmer, who stated that neither the chlorides nor the acetates could be separated by distillation. With long continued distillation, as our results will show, the crude product of the chlorination can be separated into its constituents sufficiently to yield constant boiling-points and satisfactory analytical data.

Since Beilstein[1] found that isobutane boils at —17°.5, it seemed reasonable that it should be contained in our product —10°, especially since a considerable portion of this distillate condensed below —15°. In submitting 200 grams of this distillate in several portions to the action of chlorine with all possible precautions, a considerable portion of the chlorine product was lost, probably because it consisted to a large extent of

[1] Ann. Chem. (Liebig), 144, 10.

the more volatile chlorine derivatives of propane. Although much of the unchanged hydrocarbon must have escaped with the gaseous hydrochloric acid, 100 grams remained after the chlorination, which was washed, dried and distilled. Prolonged distillation, however, failed to collect any considerable portion within sufficiently close limits to indicate the presence in appreciable quantity of an individual hydrocarbon. A small quantity, perhaps 5 grams, collected between 65° and 70°, doubtless isobutyl chloride from isobutane, which had not been completely removed into the higher fractions at 0°. But the product distributed itself along in degree fractions from 30° to 150°, at no point in quantities larger than half a gram or 1 gram.

Between —10° and —2° much smaller quantities of the hydrocarbon distillates were obtained, but within the limits —2° and 2°, 300 grams came together, and the distillate— 0°-1° gave, as its specific gravity at 0°, 0.6029, and at —12°, 0.6141. Ronalds found as its specific gravity 0.6000. A vapor-density determination gave the following value :

0.0945 gram oil gave 73.6 cc. vapor at 5°, under 370.4 mm. of mercury.

Calculated for C_4H_{10}.	Found.
2.01	2.07

In quantities of 100 grams each, the fractions —20° to 2° were converted into the chlorine derivatives. The chlorination of such a quantity is of necessity somewhat tedious ; it requires continuous operation during ten or twelve days, and it cannot be hastened, since too rapid absorption generates heat, and rapid escape of hydrochloric acid carries off the product. With care we were able to complete the absorption of sufficient chlorine without any considerable loss. In subjecting the chlorine product to fractional separation, after the fifth distillation it began to collect between 65° and 70°, and after the twentieth, 80 per cent. collected at 68°-69°. Of the remainder, 40 grams below 60° proved to consist mainly of unchanged hydrocarbon with sufficient chlorine product to raise the boiling-point. Distillation of the higher portions was continued in 1° fractions to 160°, beyond which very lit-

tle remained. To prevent a slight decomposition above 150°, at first distillation was conducted *in vacuo*, but the boiling-points soon fell below the point of decomposition. In this entire series of 1° distillates, only at 120°–121° did any appreciable quantity collect, and here only to the extent of 2–3 grams. The portions collected at other points were doubtless mixtures in very small amounts of higher chlorine products. The liquid 68°–69° was shown by analysis and vapor density to have the composition required for monochlorbutane.

I. 0.1288 gram oil gave 0.2440 gram CO_2 and 0.1166 gram H_2O.

II. 0.2025 gram oil gave 0.3845 gram CO_2 and 0.1778 gram H_2O.

III. 0.2537 gram oil gave 0.3950 gram AgCl (Carius).

IV. 0.2645 gram of the oil gave 0.4078 gram AgCl.

	Calculated for C_4H_9Cl.	Found.			
		I.	II.	III.	IV.
C	51.89	51.65	51.77	....	....
H	9.73	10.05	9.76	....	....
Cl	38.38	....	....	38.50	38.13

In a determination of its specific gravity at 24°, this butyl chloride gave 0.8690; at 27°.8, another determination gave 0.8648. The latter value agrees closely with that of Pierre and Puchot,[1] who found at 27°.8, 0.8650.

In determining its vapor density by the method of Hofmann, 0.0975 gram oil gave 65 cc. vapor at 100°, under a tension of 36.44 mm.

Calculated for C_4H_9Cl.	Found.
3.20	3.30

In further evidence of its identity, this butyl chloride was converted into the acetate by heating it twenty-four hours to 140° with fused potassic acetate and glacial acetic acid, according to the method of Schorlemmer. Upon diluting the contents of the tube, the oil which separated distilled for the most part at 116°–117°, corresponding to the boiling-point of isobutyl acetate, 116°.5. The acetate was converted into the alcohol by heating with alcoholic potassic hydrate, and its boiling-point, 107°–108°, showed it to be isobutyl alcohol,

[1] Ann. Chem. (Liebig), **163**, 276.

boiling-point 108°–109°. Upon analysis the alcohol gave the required percentages of carbon and hydrogen :

0.1737 gram substance gave 0.4090 gram CO_2 and 0.2113 gram H_2O.

	Calculated for C_4H_9OH.	Found.
C	64.86	64.22
H	13.51	13.52

Isobutyl sulphide was also prepared by boiling the chloride with an alcoholic solution of potassic sulphide. It gave the required percentage of sulphur :

0.1640 gram oil gave, by the method of Carius, 0.2631 gram $BaSO_4$.

	Calculated for $(C_4H_9)_2S$.	Found.
S	21.92	22.03

As already explained, prolonged fractional distillation failed to show the presence of any other chlorine derivative of this hydrocarbon except one that distilled tolerably constant at 121°–122°. The quantity of this product was too limited to admit of complete purification ; while the analyses showed that it still contained monochlorbutane, the results are sufficiently close to establish the presence of dichlorbutane. Since no dichlorbutane with this boiling-point has hitherto been found, it is to be regretted that our supply of material was so limited. But on account of the vast amount of labor that would be necessary to obtain an adequate quantity, it has not seemed of sufficient importance in the pressure of other portions of this work.

This substance gave the following results on analysis :

I. 0.1390 gram oil gave by combustion with plumbic chromate 0.1960 gram CO_2 and 6.1887 gram H_2O.

II. 0.2360 gram oil gave 0.5245 gram AgCl.

	Calculated for $C_4H_8Cl_2$.	Found.	
		I.	II.
C	37.79	38.46	....
H	6.30	7.08	....
Cl	55.91	....	54.94

The quantity of this product was insufficient for a determination of its specific gravity. The following value was obtained as its vapor density :

0.1655 gram oil gave 87.2 cc. vapor at 182°, under a tension of 447 mm.

Calculated for $C_4H_8Cl_2$.	Found.
4.39	4.16

Our first attempts towards separating the butanes were made before the necessity of long continued distillation was fully appreciated. Not until after several trials was it observed to what an extent a small proportion of isobutane depressed the boiling-point of pentane. In the earlier work, after 6 or 8 distillations, the product was assumed to be sufficiently pure for chlorination. A study of the chlorine derivative showed beyond question that the hydrocarbon was pentane. We were still further misled by the boiling-point of the pentyl chloride, 96°, which did not correspond to that of any hitherto published. Referring to our former notes on the vapor density of the distillate 8°–9°, we found the following determinations:

I. 0.1717 gram oil gave 45.5 cc. vapor at 16°, under a tension of 48.1 cm. of mercury.

II. 0.0849 gram oil gave 46.8 cc. vapor at 18°.5; tension, 47.75 cm.

III. 0.0999 gram oil gave 51.5 cc. vapor at 18°.5; tension, 51.75 cm.

IV. 0.0751 gram oil gave 43.5 cc. vapor at 18°.5; tension, 45.76 cm.

Calculated for		Found.			
C_4H_{10}.	C_5H_{12}.	I.	II.	III.	IV.
2.01	2.49	2.04	2.38	2.35	2.36

It will be seen that determination I corresponds closely to the composition of butane, and determinations II, III, and IV to that of pentane. When these determinations were made we expected results that would substantiate what had previously been done on the butanes, and therefore accepted only the first result, which was the last one obtained as supporting this view. But in the light of further knowledge of these bodies, the determinations thought to be erroneous correspond more nearly to pentane, although showing the influence of the small quantity of isobutane. The first result was

published in a former paper,[1] when it was assumed that we had in hand the butane which Warren had previously separated. Suspecting, therefore, the purity of our hydrocarbon distillate 8°–9°, in resuming this work the distillation was conducted with a sufficient quantity of material, and carried far enough to separate completely all fractions between 5° and 20°. In the fraction 8°–9°, after the tenth distillation, two vapor-density determinations gave, (I) 2.17, (II) 2.17. In a distillate 6°–8°, Ronalds[2] obtained as its vapor density 2.178, evidently indicating, as our values do, a mixture of butane and pentane.

But continuing this distillation in single-degree fractions, scarcely anything remained within these limits after the twentieth distillation. Having obtained the same result in several quantities of 45 liters each, collected at different dates, it became evident that neither Pennsylvania nor Ohio petroleum contains a single body with a boiling-point within these limits. Furthermore, we have not been able to detect normal butane in any of these volatile distillates. There is not the least difficulty in separating chlorine derivatives of these hydrocarbons by fractional distillation. All the chlorine products we have prepared have collected readily within the limits of temperature of their characteristic boiling-points. But in no instance in the chlorination of hydrocarbon distillates collected between —10° and 20° has a distillate collected at 77°–88°, the boiling-point of normal butyl chloride. Having excluded a constituent of Pennsylvania and Ohio petroleum within the limits mentioned above, and having observed that certain properties of isopentane derivatives are not in all respects identical with those previously published, it seemed to us of sufficient interest to devote some attention to the derivatives of this hydrocarbon. We therefore collected several hundred grams of a distillate at 29°–30°, and exposed the oil to the action of chlorine in several separate quantities until about 200 cc. of the substitution-product was obtained. In generating such large quantities of chlorine, without discomfort from leaks, we have found the large Berlin porcelain stills extremely convenient. The chlorinated product was washed,

[1] Proc. Am. Acad., **31**, 24. [2] J. Chem. Soc., 1865, p. 54.

dried, and carried through a long course of distillations, until after the eighteenth distillation it collected to the extent of 85 per cent. between 95° and 96°, under a constant tension of 730 mm., which for convenience was selected for all these distillations. In a large series of distillations a constant tension is simply and very conveniently obtained by means of the tension-regulator elsewhere described,[1] with the stopcock manipulated by a lever movable on a horizontal support. By a suitable adjustment of side tubes, stopcocks and adapters, any number of distillation-flasks may be introduced into the train, and regulated by the single stopcock. As many as fifteen distillations collecting in single-degree fractions have been in simultaneous operation with no interruption incident to changes of flasks or collection of distillates. It is quite impossible, in Cleveland, to carry on a course of distillations extending through several weeks without some form of tension-regulator, on account of sudden and extreme changes in the barometric pressure, occasionally equivalent to 25 mm. within a few hours.

Under 760 mm. and with the thermometer wholly in the vapor, chlorpentane distilled completely between 96° and 97°, for the most part at 96°.5. From a distillate below 30°, Pelouze and Cahours obtained a butyl chloride, as already mentioned, which boiled at 98°–103°.

The purity of our product is shown by analysis:

I. 0.1205 gram oil gave 0.2479 gram CO_2, and 0.1139 gram H_2O.

II. 0.2166 gram oil gave 0.2952 gram AgCl.

III. 0.2942 gram oil gave 0.4031 gram AgCl.

	Calculated for $C_5H_{11}Cl$.	Found. I.	II.	III.
C	56.33	56.13	....	....
H	10.43	10.51	....	....
Cl	33.33	....	33.69	33.88

A determination of the specific gravity of this chlorpentane at 20° gave 0.8750. Its vapor-density by the Hofmann method was found to have the following value:

0.1291 gram oil gave 72.6 cc. vapor at 100° under a tension of 384 mm.

[1] Proc. Am. Acad., 31, 10.

Calculated for $C_5H_{11}Cl$.	Found.
3.68	3.72

In forming isopentyl acetate, the purified chloride was heated 48 hours to 150°–160° with potassic acetate and glacial acetic acid. When washed, dried, and well fractioned, a small quantity collected at 134°–135° (760 mm.), which is somewhat lower than the boiling-point of isoamyl acetate, 138°.6. The amount of our material was not sufficient to raise its boiling-point, but it gave the required percentages of carbon and hydrogen.

0.1555 gram oil gave 0.3651 gram CO_2, and 0.1514 gram H_2O.

	Calculated for $C_5H_{11}C_2H_3O_2$.	Found.
C	64.60	64.00
H	10.80	10.81

When heated during several hours with alcoholic potash, the acetate was converted into the alcohol which was separated from the solution with salt. On account of the small quantity of alcohol obtained, its boiling-point could not be raised above 117°–120° (boiling-point of inactive amyl alcohol, 131°), although its composition corresponded to that of amyl alcohol.

0.1866 gram oil gave 0.4620 gram CO_2, and 0.2293 gram H_2O.

0.1854 gram oil gave 0.4610 gram CO_2, and 0.2315 gram H_2O.

	Calculated for $C_5H_{11}OH$.	Found.	
		I.	II.
C	68.18	67.51	67.81
H	13.63	13.66	13.88

At higher temperatures to 150°, the crude chlorine product could be distilled without decomposition. Above this point the residue was distilled *in vacuo*, which reduced its boiling-point to such an extent that further distillation could be carried on under atmospheric pressure, leaving only a very small residue above 150°, probably of substitution-products containing a large number of chlorine atoms.

At no point between 96° and 160° could a distillate be held constant, except at 144°–145°. Here five grams collected after

the fifteenth distillation that distilled at 144°–146°, mostly at 145°, under 760 mm. and with the mercury column wholly in the vapor. This oil proved on analysis to have the composition required for dichlorpentane.

I. 0.1309 gram oil gave 0.2055 gram CO_2, and 0.0888 gram H_2O.

II. 0.1976 gram oil gave 0.3993 gram AgCl.

	Calculated for $C_5H_{10}Cl_2$.	Found. I.	II.
C	42.56	42.84	....
H	7.09	7.54	....
Cl	50.36	....	49.96

A determination of the vapor-density of this body gave a value corresponding to dichlorpentane.

0.1680 gram oil gave 80.6 cc. vapor at 182° under a tension of 426 mm.

Calculated for $C_5H_{10}Cl_2$.	Found.
4.88	4.78

The boiling-point of this dichlorpentane is the same as that of amylene chloride, 145°, described by Bauer.[1] It is to be regretted that the quantity of our product was so limited; but on account of the great labor involved in its preparation, it did not seem advisable to attempt the preparation of a larger amount.

These results indicate that petroleum contains but one butane, and that is isobutane, which collects at 0°. That this body is not normal butane is shown by the boiling-point, 67°–68°, of the monochlor derivative, the boiling-point, 116°, of the acetate, that of the alcohol, 108°–109°, and that of the sulphide, 172°. It has hitherto been assumed that the butane in the petroleum is the normal hydrocarbon, because the butane prepared by Frankland from ethyl iodide and zinc boils at 0°. But isobutane prepared by Butlerow from tertiary butyl alcohol should boil at —17°.5. The differences between the properties of butane and isobutane are sufficiently marked to permit, without difficulty, of distinguishing between the isomeric forms.

Normal butyl chloride boils at 77°.6, and the alcohol at

[1] Ztschr. Chem., 1866, 380.

117°. Since our series of derivatives from petroleum butane was prepared several times with the same results, and never with the formation of compounds with boiling-points corresponding to normal butane, there can be no question that normal butane is not contained in Pennsylvania nor in Ohio petroleum. The series question concerns the boiling-point of isobutane which we found in petroleum. As has been fully explained, our 0° fractions were separated as many as four different times from the lightest gasoline we could procure from the refinery. While we never failed to collect distillates below —10°, they were much smaller in quantity than those in the vicinity of 0°. It is, therefore, certain that the butane we had in hand was isobutane, and it seems equally certain that this hydrocarbon collected at 0° and not at —17°.

The Octanes in Ohio Petroleum.

It has already been pointed out by one of us[1] that the published accounts of the octanes in petroleum are not fully concordant. Pelouze and Cahours first announced in their series of hydrocarbons an octane, boiling-point 116°–118°, and a little later Schorlemmer[2] found a body in coal-tar distilling at 119°–122°, and another at 124°, both with the composition required for octane. Possibly led to believe by the results of Beilstein and Kurbatoff that the distillate 119°.5–122° is hexahydroisoxylol, in his latter summation of the octanes known, Schorlemmer seems to repudiate the one boiling at 119°–122°, which he had previously described. Warren recognized two octanes, one boiling at 119°.5, and another boiling at 127°.6. These bodies were identified alone by vapor-density determinations and boiling-points; no analyses were given. In the separation of the hydrocarbons resulting from the distillation under pressure of menhaden oil, Engler discovered the octane di-isobutyl, boiling-point 109°. In support of the work of Pelouze and Cahours, Lemoine[3] submitted American ligroïn to *four* fractional distillations, collecting distillates within limits of *five* degrees, and separated an octane, boiling-point 121° at 779 mm. In our experience, the hydrocarbons in

[1] C. F. M., *loc. cit.*

[2] J. Chem. Soc., **15**, 419.

[3] Bull. Soc. chim. (Paris), **41**, 161.

petroleum with boiling-points not far removed can only be separated by the use of the best possible means for fractional separation, in a long course of distillations. The separation of the octanes, for example, requires a refinery distillate boiling between 120° and 170°, and it is not until the twentieth distillation that the octanes begin to accumulate with any degree of purity. In all our experiments after the fifth distillation, the octanes are still contained for the most part in the portions above 125°, and they are separated very slowly into their respective fractions. In undertaking further study of the octanes in Ohio petroleum, we procured from the refinery of Messrs. Schofield, Shirmer, and Teagle, 72 liters of a burning oil distillate that distilled in our hands, within the limit of ten degrees, in the following proportions:

	−75°	75°-100°	100°-110°	110°-120°	120°-130°	130°-140°	140°-150	150°-160°	+160
Liters	10	12	10	8	8	8	5	5	5

The sulphur compounds were precipitated from these fractions by means of alcoholic mercuric chloride, the oils washed and dried, and the distillation continued within limits of 5°, 2°, and finally within 1°, under a constant tension of 730 mm. In further explanation of what was said above concerning the slow separation of these constituents, the following record of the tenth distillation is given; when it is borne in mind that these weights are from 65 liters, the small amounts of the constituents will be appreciated:

	115°-116°	116°-117°	117°-118°	118°-119°	119°-120°	120°-121°	121°-122°
Grams	60	60	80	100	145	130	160

	122°-123°	123°-124°	124°-125°	125°-126°	126°-127°	127°-128°	128°-129°
Grams	120	170	160	150	120	90	40

If the distillation had been stopped at this point, since on account of the diminished tension the true boiling-points should be at least one degree higher than those given, it might be inferred that one of the principal constituents was a hydrocarbon boiling at 126°–127°.

No doubt this inference would be supported by the vapor-density of this product, but further distillation showed its fallacy. At the end of the thirty-third distillation, 190 grams collected at 118°.5–119°.5, which distilled between 119°.5–120°,

for the most part at 119°.5, under 760 mm. with the mercury column wholly in the vapor. Its specific gravity at 20° was found to be 0.7243. This liquid was assumed to have the same composition as the octane whose identity was shown by analysis and a vapor-density determination.

The vapor-density of this product was found to support the same composition:

0.1287 gram oil gave 75 cc. vapor at 182°, under a tension of 429 mm.

Calculated for C_8H_{18}.	Found.
3.95	3.91

The specific gravity of the crude distillate was found to be 0.7256. The presence of this hydrocarbon is still furthur assured by the prolonged distillation. Our boiling-point is practically the same as that of Warren, although his product from Pennsylvania petroleum must have been contaminated to some extent by hexahydroisoxylol, which was not shown to be present in Pennsylvania oil until long after the work of Warren was completed. Our boiling-point was taken in a portion of the Ohio oil which had been subjected to prolonged treatment for the removal of hexahydroisoxylol. The specific gravity of this distillate purified by fuming sulphuric acid with the aid of heat was 0.7230. Another portion purified with a mixture of nitric and sulphuric acids, gave as its specific gravity 0.7190. In the oil with the same boiling-point separated from coal-tar, Schorlemmer found the specific gravity 0.7190 at 17°.5. In our product purified with fuming sulphuric acid, the required percentages of carbon and hydrogen were obtained:

0.1475 gram oil gave 0.4562 gram CO_2, and 0.2073 gram H_2O.

	Required for C_8H_{18}.	Found.
C	84.22	84.35
H	15.80	15.62

In the formation of chlorine derivatives from this octane, the same method was employed without cooling as in the case of the more volatile distillates. It was ascertained that the best yield of monochloroctane was given when the quantity of

[1] Mabery: *Loc. cit.*

chlorine absorbed was 50 per cent. in excess of the amount theoretically required to form the monochlor derivative. Even with this excess, still a small amount of the hydrocarbon remained unchanged. Since it was found that the chlorinated compound could not be distilled under atmospheric pressure without serious decomposition, after washing and drying it was fractioned *in vacuo* under a tension of 50 mm., within limits of 10°, 5°, 2°, and finally for some time within 1°. Under 50 mm. fractions collected at all points between 65° and 150°, but a larger quantity at 83°–84°, which under atmospheric pressure, distilled at 164°–166°. The composition of this substance was determined by analysis :

I. 0.1479 gram oil gave 0.3523 gram CO_2, and 0.1537 gram H_2O.

II. 0.1961 gram oil gave 0.1888 gram AgCl.

III. 0.2483 gram oil gave 0.2408 gram AgCl.

	Calculated for $C_7H_{17}Cl$.	Found. I.	II.	III.
C	64.65	64.95	....	....
H	11.45	11.54	....	....
Cl	23.90	....	23.81	23.97

A determination of vapor-density gave a value required for monochloroctane :

0.1682 gram oil gave 78 cc. vapor at 182° under a tension of 400 mm.

Required for $C_8H_{17}Cl$.	Found.
5.14	5.28

The monochloroctane obtained by Pelouze and Cahours,[1] and by Schorlemmer,[2] from petroleum octane, boiling-point 168°–172°, was evidently a mixture of the two chloroctanes from the hydrocarbons 119°.5 and 124°. It could not be otherwise, on account of the imperfect separation of the hydrocarbons. In our experience, nothing less than thirty distillations is sufficient for the separation of these bodies with any degree of purity.

In comparing the results in this paper with those of others, it should be borne in mind that our products were separated from Trenton limestone petroleum, which was unknown at

[1] Jsb. 1863, p. 528. [2] Ann. Chem.. (Liebig), 128, 112.

the time of the earlier study of Pennsylvania oil. But there can be little doubt that these portions of Pennsylvania and Ohio oils are identical so far as the principal constituents are concerned. That this is true of constituents with boiling-points above 150° will be shown in another paper.

In many instances, even after the most careful purification, the specific gravity of the petroleum hydrocarbons is somewhat higher than that of the same hydrocarbons synthetically prepared. Schorlemmer[1] thought this was due to fine differences of isomerism. But this was before the discovery of naphtenes in petroleum. It now seems very probable that the higher specific gravity is due to the difficulty in removing the last trace of these bodies, especially since a small excess of carbon and a slight deficiency in hydrogen for the formula C_nH_{2n+2} accompanies the higher specific gravity. A notable quality of the naphtenes is their inertness toward reagents, which is doubtless greatly increased by large dilution in the principal petroleum hydrocarbons.

In Russian petroleum, Markownikoff[2] and Putochin discovered isoctonaphtene, boiling-point 122°.5. In looking for this hydrocarbon in Ohio petroleum the fractions 120°–124° were carefully distilled many times, until so little remained within these limits that no individual constituent could be present in any appreciable quantity, or in such quantity that it could be collected by fractional distillation and identified. The octane found by Lemoine at 121° is, therefore, also excluded.

The octane, boiling-point 125°.46, separated by Schorlemmer, was assumed to be identical with normal octane formed from normal butyl iodide by the action of sodium. Warren found a somewhat higher boiling-point for the octane from Pennsylvania petroleum. This body distilled between 126°.8 and 129°.1, or in the mean at 127°.6; its composition was based upon a determination of its vapor-density, but it was not supported by analysis. The observations of Warren were apparently confirmed by similar distillates separated from Ohio and Canadian petroleum.[3] Distillates collected at 126°–127° from these oils after the eleventh fraction gave

[1] Phil. Trans., 171, 451, (1880). [2] Ber. Chem. Ges., 18, 1880.
[3] Mabery: Proc. Am. Acad., 31, 32, 57.

values in vapor-density determinations corresponding to that of octane. But evidently such determinations, unsupported by other data, are less reliable, especially in products not far removed in boiling-points from other isomers. Although our former results apparently confirmed the presence of an octane at 129°–127°, those values were accepted as provisional, to be supported or modified by more prolonged distillations which have now been made.

Under a constant tension of 730 mm., forty-two distillations were made between 121° and 130° through Hempel bead columns. Of the last distillates scarcely any remained at 126°–127°, or between this point and 130°, and very little at 125°–126°. The greater portion, 200 grams, collected at 124°–125°, normal conditions. There is, therefore, in Ohio petroleum, no octane with a boiling-point higher than 125°. After purification with a mixture of nitric and sulphuric acids, and sodium, the distillate 124°–125° was shown by analysis to have the composition for octane :

0.1471 gram oil gave 0.4544 gram CO_2, and 0.2077 gram H_2O.

	Calculated for C_8H_{18}.	Found.
C	84.22	84.26
H	15.79	15.70

After thorough treatment with fuming sulphuric acid, this octane gave 0.7183 as its specific gravity. Another portion, carefully purified with a mixture of nitric and sulphuric acids gave 0.7134. The specific gravity of the synthetic hydrocarbon was given by Thorpe as 0.7188. The crude distillate, with no purification, gave as its specific gravity 0.7243. Its vapor-density was found by the method of Hofmann.

0.1578 gram oil gave 84.4 cc. vapor at 182°, under a tension of 462 mm.

Calculated for C_8H_{18}.	Found.
3.95	3.96

In the formation of monochloroctane from this distillate, the hydrocarbon was exposed to the action of chlorine in the cold until the increase in weight was fifty per cent. in excess of the quantity theoretically required to form monochloroctane. The product, containing a small amount of the hydrocarbon

still unchanged, was washed, dried, and submitted to fractional distillation *in vacuo* under 50 mm., since it was found that it could not be distilled under atmospheric pressure without decomposition. A considerable portion collected at 89°–91°, that distilled under atmospheric pressure, normal conditions, at 173°–174°. Schorlemmer stated that chlorine converts normal octane into a mixture of primary octyl chloride, boiling-point 179°–180°, and secondary octyl chloride boiling at 175°. None of our product collected at the point corresponding to the normal chloride, although the quantity was not sufficient to determine the boiling-point with absolute precision, and not sufficient to form other compounds. Pelouze and Cahours[1] gave 168°–172° as the boiling-point of the chloride which they formed from petroleum octane, but their hydrocarbon was evidently not fully purified.

This substance gave upon analysis percentages of carbon, hydrogen, and chlorine required for chloroctane :

I. 0.1222 gram oil gave 0.2880 gram CO_2, and 0.1264 gram H_2O.

II. 0.1821 gram oil gave 0.1792 gram AgCl.

III. 0.2203 gram oil gave 0.2200 gram AgCl.

	Calculated for $C_8H_{17}Cl$.	Found. I.	II.	III.
C	64.65	64.27	....	....
H	11.45	11.19	....	....
Cl	23.90	....	24.33	24.69

A determination of vapor-density gave a value required for chloroctane :

0.1675 oil gave 76 cc. vapor at 182°, under a tension of 418 mm.

Calculated for $C_8H_{17}Cl$.	Found.
5.14	5.16

The small amount of distillates above 91° *in vacuo* showed the presence in minute proportions of higher chlorinated products, but it would require much larger quantities than we could conveniently procure to ascertain their composition.

Since Engler[2] discovered tetramethylbutane or diisobutyl, boiling point 108°.5, as one of the products in the distillation

[1] Jsb., 1863, p. 528. [2] Ber. d. Chem. Ges., **22**, 592.

of fats under pressure, with the possibility that this body might be present in Ohio petroleum, we submitted the portions of this petroleum distilling between 100° and 115° to prolonged distillation within single-degree limits. But after treatment with nitric acid, no distillate collected in this vicinity. Having in hand a series of fractions near 135°–136°, the boiling-point of hexahydromesitylene, or nononaphtene, they were carried through a long course of distillations, and the small amount remaining within these limits was examined with the aid of fuming nitric acid and fuming sulphuric acid, but no sulphonic acid was formed, and the very small amount of nitro compound was not sufficient for a melting-point determination.

In view of the fact that the series of petroleum hydrocarbons boiling approximately at 38°, 68°, and 98°, has received little attention since it was first discovered by Warren, I shall soon undertake an examination of these bodies, and also of petroleum nonane to which Warren assigned the boiling-point 151°.

C. F. M.

Contributions from the Chemical Laboratory of Cornell University.

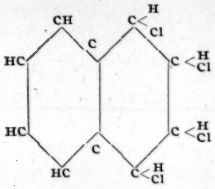
NAPHTHALENE TETRABROMIDE, $C_{10}H_8Br_4$.

By W. R. Orndorff and C. B. Moyer.

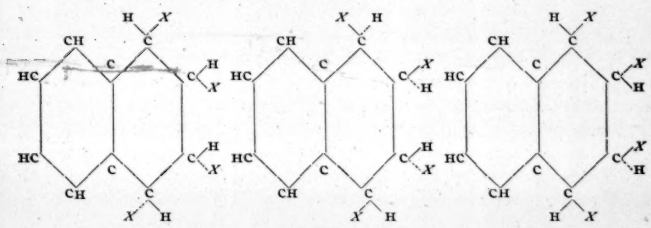
The chlorine addition-product of naphthalene, known as naphthalene tetrachloride, $C_{10}H_8Cl_4$, has been known for some time, having been prepared by Laurent[1] in 1833, and having since been studied by E. Fischer,[2] Leeds and Everhart,[3] Atterberg[4] and others.

The corresponding tetrabromide, $C_{10}H_8Br_4$, has not yet been made, so far as we are aware. These two substances are exceedingly interesting from the standpoint of stereochemistry. Assuming that in naphthalene tetrachloride the halogen adds itself to only one of the benzene residues, an assumption that is proved to be correct by the fact that this tetrachloride yields only phthalic and oxalic acids on oxidation, we have the following structural formula for this substance :

[1] Ann. chim. phys. [2], **52**, 275; [2], **59**, 196.
[2] Ber. d. chem. Ges., **11**, 735, 1411.
[3] J. Am. Chem. Soc., **2**, 205.
[4] Ber. d. chem. Ges., **11**, 1223.



Theoretically there should be three stereoisomers having this structural formula, as follows:



1. 2. 3.

In these formulas the dotted lines are intended to represent positions below the plane of the paper, while the unbroken lines represent those above this plane. Thus in formula 1 the halogen atoms, represented by the letter *X*, are all below the plane of the paper and the hydrogen atoms are above. This is the cis-form according to the nomenclature of von Baeyer. Formulas 2 and 3, both of which represent the trans-forms, are not identical, since they cannot be made to coincide, but represent enantiomorphous forms, and if they could be obtained in crystals, would probably be found to crystallize enantiomorphous.

These stereo-formulas are the only ones possible for the tetrahalogen addition-products of naphthalene where all the halogen atoms attach themselves to only one benzene ring.

Two naphthalene tetrachlorides have been described in the literature. The tetrachloride melting at 182° C. and formed by the action of chlorine on melted naphthalene has long been known. The other tetrachloride, generally called the

β-compound to distinguish it from the α-product melting at 182° C., was first made by Laurent[1] in 1850, and afterwards by E. Fischer.[2] The latter obtained this compound together with the α-tetrachloride, by the action of potassium chlorate and hydrochloric acid on naphthalene. The two substances were separated by their difference in solubility in alcohol, the β-product being very soluble, while the α-product is only slightly soluble in this solvent. An analysis of the compound is given and the melting-point is stated to be 116°–118° C. It differed markedly from the α-tetrachloride in being very soluble in both alcohol and ether. During the same year, 1878, Atterberg published a short criticism of Fischer's paper, stating that he had made a special study of the action of chlorine on naphthalene and had sought in vain to isolate the β-naphthalene tetrachloride described by Fischer, and suggesting that the compound might have been dichlornaphthalene dichloride. Fischer, answering this article, adhered to his former opinion, and stated his intention to pursue the matter further at an early date; but up to the present he has published nothing further on this subject.

Naphthalene tetrachloride, made in several different ways, has been carefully examined by Mr. D. A. Morton, one of the advanced students in this laboratory, in order to see if it could be obtained in more than one form. It was not found possible, however, to make an addition-product differing in any way from the α-product melting at 182° C., nor could this product be separated into two substances by any of the methods made use of. An oily product was obtained in the preparation of the tetrachloride by the method given by E. Fischer, which gave off hydrochloric acid when heated; but whether this was a new tetrachloride or only a monochlornaphthalene containing some dissolved naphthalene tetrachloride or naphthalene dichloride could not be determined.

Three tetrabromides of α-nitronaphthalene as well as two dibromnaphthalene tetrabromides have been prepared by Guareschi,[3] and as it seemed highly probable that naphthalene itself would yield addition-products with bromine, the follow-

[1] Compt. rend. des Travaux de chimie, 1850, 1: Ann. Chem. (Liebig), **76**, 298.
[2] Ber. d. chem. Ges., **11**, 735.
[3] Ann. Chem. (Liebig), **222**, 285; Gaz. chim. ital., **16**, 142.

ing investigation was undertaken to see if naphthalene tetrabromide could be made, and if so, whether it existed in more than one stereochemical modification. The preliminary part of this work was done by Dr. F. K. Cameron, now of the Catholic University of Washington, who not only found that naphthalene tetrabromide could be made by the addition of bromine to naphthalene, but also succeeded in isolating a small quantity of the product and identifying it by a determination of the amount of bromine it contained.

Method of Preparation of Naphthalene Tetrabromide.

The method used in preparing the naphthalene tetrabromide was as follows: 100 grams of finely powdered *pure* naphthalene were placed in an Erlenmeyer flask, together with some cracked ice and a small quantity (200 cc.) of a 4 per cent. solution of sodium hydroxide. The flask was then surrounded with ice water and 150 grams of bromine were run in slowly from a dropping-funnel,[1] the lower end of which was drawn out to a very narrow opening, and which dipped below the surface of the liquid in the flask. The flask was shaken constantly during the addition of the bromine, and the ice in the flask replaced by a fresh supply as it melted. Little or no hydrobromic acid was given off under these conditions and complete addition of the bromine to the naphthalene seemed to have taken place, a deep-red, pasty mass resulting. The flask and its contents were allowed to stand in a cool place for a few hours—generally over night. The water was then decanted from the pasty mass, which was afterwards ground up and thoroughly washed with cold water. It was then treated repeatedly with small quantities of luke-warm alcohol, which extracted the unchanged naphthalene, the α-monobromnaphthalene and the 1-4 dibromnaphthalene. After repeated extractions in this manner, a small quantity of a white solid was obtained, which was but slightly soluble in alcohol and which melted at 116°–120° C. This was then recrystallized several times from chloroform, yielding a transparent, colorless, well crystallized product, melting at 111° C. The yield was about seven grams.

[1] The bromine in the dropping-funnel was kept covered with ice water to prevent evaporation and also to keep the bromine cold.

A determination of the amount of bromine in this purified product by the Carius method gave the following results: [1]

I. 0.1780 gram of the substance gave 0.3031 gram of AgBr.

II. 0.2173 gram of the substance gave 0.3662 gram of AgBr.

	Calculated for $C_{10}H_8Br_4$.	Found.	
		I.	II.
Bromine	71.42	72.47	71.69

The results obtained by Dr. Cameron with the product isolated by him were as follows:

0.2634 gram substance gave 0.4443 gram AgBr.

	Calculated for $C_{10}H_8Br_4$.	Found.
Bromine	71.42	71.67

As the product was made from naphthalene by the addition of bromine and was undoubtedly a tetrabrom addition-product, it was not thought necessary to determine the amounts of carbon and hydrogen it contained.

The heavy oily portions extracted by the warm alcohol were put together, and, after most of the solid matter had been crystallized out by cooling in a freezing-mixture, the alcohol was evaporated and the residue subjected to distillation in superheated steam. The first substance to distil was unchanged naphthalene, then α-monobromnaphthalene and finally 1 : 4 dibromnaphthalene. On redistilling the oily α-bromnaphthalene alone it bumped violently and gave off both bromine and hydrobromic acid, indicating the presence of an addition-product; but whether this was due to some of the solid naphthalene tetrabromide being dissolved in the oily bromnaphthalene, or to an oily tetrabromide or to a dibrom addition-product, could not be ascertained, as it was not found possible to isolate any pure substance from the product save the α-monobromnaphthalene.

Numerous modifications of the method were tried with a view of increasing the yield of the tetrabromide, but in none of these was the yield increased, nor could any other tetrabromide be isolated.

[1] In calculating these results we used the following atomic weights: Ag, 107.92; Br, 79.95; C, 12.01; H, 1.008, taken from Clarke's Constants of Nature, 1897.

Properties of the Naphthalene Tetrabromide.

The tetrabromide made by the above method is a solid melting at 111° C., with decomposition, giving off bromine and hydrobromic acid. It is insoluble in water, ether, glacial acetic acid and cold alcohol; very slightly soluble in hot alcohol, and readily soluble in carbon disulphide, ligroïn, hot chloroform, and hot benzene. It crystallizes in transparent monoclinic prisms, which become opaque on standing in the light, or when heated, this opaqueness probably being due to surface evaporation from the crystals. When kept in the dark and in a tolerably cold room they preserve their transparency and brilliancy for some time; but eventually become opaque and assume a red color from the separation of the bromine.

A large number of the crystals carefully recrystallized from chloroform were examined by Professor A. C. Gill, of the Mineralogical Department of this University, to whom we are much indebted for the following report:

"The brilliant, colorless crystals of naphthalene tetrabromide are very variable in shape, usually flattened parallel to a prism face. From measurements on about fifteen crystals, most of which were one to two mm. in diameter, the crystal system was determined to be monoclinic, with the following angles and axial ratios:

$\beta = 67° 3'$ $\quad$ $\dot{a} : \dot{b} : \dot{c} = 1.2075 : 1 : 1.4775.$

Angles.	Calculated.	Found.	Number of observations.
001 : 110		74° 53′	11
001 : $\bar{1}$01		65° 06′ 30″	14
$\bar{1}$01 : $\bar{1}$11		47° 36′ 30″	6
110 : 1$\bar{1}$0	96° 04′	96° 02′	10
001 : 101	37° 20′	37° 21′ 40″	6
001 : 011	53° 41′	53° 38′	2
$\bar{1}\bar{1}$1 : $\bar{1}\bar{1}$0	31° 36′	31° 37′	7
001 : $\bar{1}$11	73° 31′	73° 30′	12
$\bar{1}$11 : 011	40° 15′ 30″	40° 23′	1

Of the six forms included in this list, the prism, 110; the base, 001; and the positive orthodome, 101, are usually the principal faces of the crystals. The other three forms occur as modifications on the edges and angles.

The accompanying figures show two of the most common shapes of the crystals.

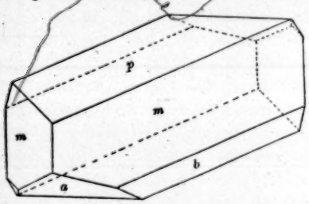


Fig. 1.

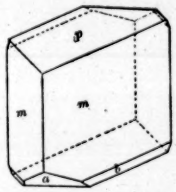


Fig. 2.

$p = (001)$, $m = (110)$, $a = (10\bar{1})$, and $b = (11\bar{1})$.

The question whether the tetrabromide of naphthalene is isomorphous with the tetrachloride must be looked upon as undecided. There is a close resemblance between the angle β of the two substances; for the former it is 67° 3′, and for the latter 67° 19′. But in order to show further likeness in the crystallographic elements, it is necessary to assume that the prevailing parameter on the vertical axis of the tetrabromide is $\frac{2}{3}$, and, on the clinoaxis is 2. This rather forcible assumption would give:

$$\dot{a} : \bar{b} : \dot{c}$$

0.8050 : 1 : 0.7388 for the tetrabromide,

and 0.7715 : 1 : 0.6921 for the tetrachloride.

This is after all not a very close agreement."

A very small quantity of the dibromnaphthalene existing in the tetrabromide will cause the crystals of the latter to become elongated along one edge. These elongated crystals were at first thought to be a second tetrabromide, but on examination by Dr. Gill, they were found to be identical with the other crystals.

Many attempts were made to separate from this tetrabromide a stereoisomer by using various solvents, some of which were optically active, but without success.

When the tetrabromide was heated in a test-tube several degrees above its melting-point, in a sulphuric acid bath, bromine and hydrobromic acid were given off, the resulting

product being a red oil. This oil was soluble in cold alcohol and on evaporation a small portion of a solid, which proved to be 1-4 dibromnaphthalene, came down first, and then a light yellow oil, which was identified as the α-monobromnaphthalene.

When the tetrabromide is boiled with an alcoholic solution of potassium hydroxide for a couple of hours it is completely decomposed. The product consists mainly of an oil which was identified as α-bromnaphthalene.

On oxidation with nitric acid the only product that could be identified was phthalic acid.

Two attempts were made to determine the molecular weight of the naphthalene tetrabromide, using the boiling-point method and chloroform and carbon disulphide as solvents; but even in these low-boiling solvents decomposition takes place, both hydrobromic acid and bromine being evolved. The first pellet introduced into the boiling liquid in both cases produced a fall instead of a rise of temperature, so that the results were valueless. It was then thought that the molecular weight of the tetrabromide might be deduced from the molecular weight of the naphthalene tetrachloride. In making all these molecular weight determinations the boiling-point apparatus devised by Orndorff and Cameron[1] was used.

A determination of the molecular weight of some of the pure naphthalene tetrachloride made by Mr. D. A. Morton, gave the following results:

Naphthalene Tetrachloride, $C_{10}H_8Cl_4 = 270$.

Solvent: Chloroform. Boiling-point 60°.2 C. at 741.7 mm. Molecular elevation for 100 grams 36°.6.

Grams solvent.	Grams substance.	Concentration in 100 grams.	Rise observed.	Molecular weight.
186.77	0.6008	0.3108	0.040°	284.5
	1.2548	0.6718	0.079	311.2
	1.8890	1.0114	0.110	336.5
	2.4779	1.3267	0.140	346.8
	3.0584	1.6375	0.179	334.8
Molecular weight at infinite dilution				**276**
Barometer constant.				

[1] This JOURNAL, 17, 517.

Grams solvent.	Grams substance.	Concentration in 100 grams.	Rise observed.	Molecular weight.
202.22	0.6041	0.2987	0.052°	210.2
	1.1597	0.5735	0.090	233.2
	1.8410	0.9104	0.130	256.3
	2.4701	1.2215	0.170	262.9
	3.1011	1.5335	0.220	255.1

Molecular weight at infinite dilution 208

Barometer constant.

The erratic results in these determinations of the molecular weight of the tetrachloride are caused by a slight decomposition of the tetrachloride, as shown by the evolution of hydrochloric acid during the determinations, and by the difference in the melting-point of the substance before and after the determinations. The tetrachloride before being used melted sharply at 180° C., and after the experiment at 165°–169° C.

The results show clearly, however, that the molecular weight of the tetrachloride is approximately 270, and that the formula of the substance is $C_{10}H_8Cl_4$, and in all probability that the formula of the tetrabromide is $C_{10}H_8Br_4$.

Regarding the stereochemical formulas of the naphthalene tetrachloride and tetrabromide, it seems quite likely from the fact that they both crystallize in the monoclinic system, that the space formula which best represents the position of the atoms in both substances, is either formula 2 or 3 given above, or they may be a mixture of both substances represented by these formulas, since it would be impossible to separate a mixture of this sort by any method now known to us.

Further work on the chlorine and bromine addition-products of naphthalene and its derivatives is already under way in this laboratory.

CORNELL UNIVERSITY,
FEBRUARY, 1897.

Contributions from the Chemical Laboratory of Harvard College.

XCVIII. — ON HYDROCOBALTOCOBALTICYANIC ACID AND ITS SALTS.

By C. Loring Jackson and A. M. Comey.

The work described in this paper was undertaken in the hope of preparing, from potassic cobalticyanide, compounds analogous to the nitroprussides. The prospect of obtaining this result was not very good, as the only previous statement about the action of nitric acid on potassic cobalticyanide was that of Zwenger,[1] who says: "Beim Kochen (of hydrocobalticyanic acid) mit Salpetersäure tritt gleichfalls keine Zersetzung ein, und man kann sie selbst auffallender Weise mit rauchender Salpetersäure anhaltend erhitzen ohne dass dadurch eine Zerstörung erfolgt." Nevertheless, it seemed to us worth while to repeat the experiment. Accordingly, we boiled about 75 to 100 cc. of a strong solution of potassic cobalticyanide with its own volume of common strong nitric acid in an open flask. At first it seemed as if Zwenger's statement was correct, as the mixture underwent no apparent change during the first three minutes, but in less than five minutes the liquid turned red, and this color increased in intensity as the boiling was continued. After boiling for about two hours the dark red solution was suddenly converted into a semi-solid gelatinous mass. On one occasion, when the quantity of solution was larger than usual, and the heat was not moderated soon enough, the reaction was so violent as to throw a large part of the gelatinous substance out of the flask in which the process was carried on. This red gelatinous product was purified by heating it with a little more nitric acid on the water-bath, and, after breaking up the lumps as thoroughly as possible, washing it with a large amount of water. As the impurities were removed the substance began slowly to go into solution, and this generally indicated that it was pure; but, if it was necessary to wash it longer, this could be done by evaporating the moist precipitate to dryness on the water-bath, which rendered it insoluble again. It was found in the preparation of the substance that essentially all the cobalt had remained in the precipitate, the first filtrate containing only

[1] Ann. Chem. (Liebig), 62, 161.

nitric acid, potassic nitrate, and hydrocyanic acid. The insoluble jelly was dried *in vacuo* for analysis, when it changed from red to a grayish-green color, but this dried salt is very hygroscopic, absorbing water rapidly from the air and regaining its red color. In fact it is so sensitive to moisture that it could be used as a very delicate test for the presence of aqueous vapor.

In analyzing the substance we first made a combustion of it in an open tube. This gave us the carbon, and also the amount of water, which we did not dare to determine by loss, as there was danger of a loss of hydrocyanic acid at the same time. As the substance contained potassium, a portion of the carbonic dioxide remained in the residue as potassic carbonate. To determine this the contents of the boat were transferred to a flask, and heated with dilute sulphuric acid, the carbonic dioxide set free, being swept out by a stream of dry air through a drying tube and the absorption bulbs. The solution of cobaltous sulphate and potassic sulphate left in the flask was then worked up with ammonic sulphide in the usual way, and the two metals weighed as sulphates. This method gave excellent results because the substance burnt quietly without any spirting, so that the whole of the inorganic matter was left in the boat.

Each of the following analyses was made with an entirely different preparation :

I. 0.2536 gram of the salt gave 0.2346 gram of carbonic dioxide and 0.0200 gram of water. Also 0.2281 gram of cobaltous sulphate. The potassic sulphate was not determined.

II. 0.2458 gram of the salt gave 0.2272 gram of carbonic dioxide, 0.0178 gram of water, and 0.0400 gram of potassic sulphate.

III. 0.2496 gram of the salt[1] gave, when evaporated with sulphuric acid, 0.2245 gram of cobaltous sulphate and 0.0408 gram of potassic sulphate.

IV. 0.2403 gram of the salt[1] gave 0.2143 gram of cobaltous sulphate and 0.400 gram of potassic sulphate.

[1] In these two analyses the amount of water was determined by the loss on heating. The percentages obtained were 0.97 and 1.05, both of which are somewhat too high because hydrocyanic acid was also given off, as was shown by the smell.

	Calculated for $KH_3Co_3(CN)_{11}H_2O$.	Found. I.	II.	III.	IV.
Carbon	25.28	25.24	25.21	....	....
Hydrogen	0.77	0.88	0.80	....	....
Cobalt	33.90	34.24	....	34.24	33.94
Potassium	7.49	....	7.31	7.34	7.47

These analyses establish the composition of this salt and are confirmed by those of the other salts given later in this paper. We have assigned provisionally to the acid, $H_3Co_3(CN)_{11}$, from which this salt is derived, the name hydrocobaltocobalticyanic acid. This salt therefore is the monopotassic cobaltocobalticyanide.

Properties of Monopotassic Cobaltocobalticyanide, $KH_3Co_3(CN)_{11}H_2O$.—This substance, as first obtained in the moist state, appears as a red jelly a little duller in tint than currant jelly. When its solution is evaporated to dryness on the water-bath, it forms a reddish-brown mass looking like shellac, which by the action of water is converted into a brownish red powder. When dried *in vacuo*, or at 100°, it becomes grayish-green, but takes up water with great avidity, regaining its red color. Its behavior toward water is peculiar. The crude product is insoluble in cold water and nearly so in hot, but, after the impurities have been washed out, it usually dissolves slowly and to a limited extent in cold water, although its behavior varies in different specimens; thus, one after standing with cold water for two weeks imparted a slight red color to the liquid, while another, which stood for two months, did not color it at all. On the other hand, digestion with a small amount of water at 60° brings it completely into solution. The speed, with which this solution takes place, depends on the treatment the gelatinous substance has received; if it had been allowed to remain for some time suspended in water, it dissolved very slowly, taking several days for complete solution; if it had been filtered out and dried, it began to dissolve in a very few minutes; yet even in this case it took from twelve to forty-eight hours to dissolve 2 grams completely. The dark-red solution thus obtained can be concentrated without depositing any of the salt; in fact this only begins to appear as the solution runs to dryness. If the residue, which looks like shellac, is covered with cold water,

it decrepitates with a series of insignificant explosions to a red powder, which is essentially insoluble in cold water, so that it can be washed with a large amount of it without perceptible loss; but, if it is digested with a small amount of water at 60°, it gradually dissolves, forming a solution in all respects like that obtained from the original product. The solution has a strong acid reaction, and gives precipitates with the salts of many of the metals as follows:

With a salt of barium, calcium, zinc, or manganese, a salmon-colored precipitate.

With ferric chloride, a yellowish-brown precipitate.

With ferrous sulphate, light-yellow.

With a salt of nickel, grayish-yellow.

With a salt of cobalt, flesh color.

With a salt of copper, greenish-blue.

With a salt of silver, salmon-colored.

With a salt of lead, a slight yellow precipitate.

With a salt of magnesium or mercury, no precipitate.

The aqueous solution was not precipitated by alcohol alone, but if a salt of potassium was also added, the dipotassic salt was precipitated.

Dipotassic Cobaltocobalticyanide, $K_2HCo_2(CN)_{11}.2H_2O$.—This salt was made by mixing a solution of the monopotassic salt and potassic acetate and then adding enough alcohol to precipitate it. The salt appeared as a pink, flocculent precipitate, which dissolved in cold water only after long standing, but quickly and easily in hot water. It is insoluble in alcohol. For analysis it was dried *in vacuo*:

0.2240 gram of the salt gave 0.1770 gram of cobaltous sulphate and 0.0684 gram of potassic sulphate.

	Calculated for $K_2HCo_2(CN)_{11}.2H_2O$.	Found.
Cobalt	30.61	30.08
Potassium	13.52	13.72

We have not yet succeeded in preparing the tripotassic salt, but think this might be done after a more careful study of the conditions of its formation.

An especially careful study of the barium and the silver

salt was made in order to establish more firmly the composition of this series of compounds.

Baric Cobaltocobalticyanide, $BaHCo_3(CN)_{11}.1\frac{1}{2}H_2O$. —This salt was made by adding an excess of baric nitrate or chloride to the solution of the monopotassic salt. The precipitate, which is soluble in an excess of the potassium salt, was purified by washing with water, dried at 180°, and analyzed with the following results:

I. 0.2698 gram of the salt gave on combustion 0.2024 gram of carbonic dioxide, 0.0156 gram of water, 0.2004 gram of cobaltous sulphate, and 0.0997 gram of baric sulphate.

II. 0.3027 gram of the salt gave 0.2294 gram of cobaltous sulphate and 0.1134 gram of baric sulphate.

	Calculated for $BaHCo_3(CN)_{11}.1\frac{1}{2}H_2O$.	Found. I.	Found. II.
Carbon	21.02	20.46	....
Hydrogen	0.64	0.64	....
Cobalt	28.18	28.23	28.19
Barium	21.82	21.72	21.82

It is a striking fact that this salt retains the 1.5 molecules of water of crystallization even at the high temperature of 180°. Its behavior, when heated, was peculiar. At 100° it turned slate color, at 180° it was a dull slate blue, and at 225° it took on a pure, clear blue color. It was evident, however, that the salt was decomposed at 225°, since on exposure to the air the blue substance turned to a pale, reddish-brown, distinctly different from the salmon color of the original salt, and when it was treated with water a gas was given off with an odor similar to that of hydrocyanic acid, but not identical with it, whereas the barium salt is not decomposed by water. This decomposition of the barium salt at 225° was accompanied by a slow but long-continued loss of weight.

The barium salt, when washed free from impurities, dissolved in water, but, when obtained by the evaporation of its solution to dryness on the water-bath, it became insoluble even in hot water.

Argentic Cobaltocobalticyanide, $Ag_3Co_3(CN)_{11}.H_2O$.—This salt was made by adding a large excess of argentic nitrate to the solution of the monopotassic salt. It was a salmon

colored precipitate, which was purified by washing with water. It was dried *in vacuo* for analysis:

I. 0.2254 gram of the salt gave 0.1392 gram of carbonic dioxide, 0.0084 gram of water, 0.1309 gram of cobaltous sulphate, 0.1154 gram of argentic chloride, and 0.0020 gram of silver.

II. 0.3094 gram of the salt gave 0.1910 gram of carbonic dioxide, 0.0082 gram of water, 0.1774 gram of cobaltous sulphate, 0.1624 gram of argentic chloride, and 0.0012 gram of silver.

	Calculated for $Ag_3Co_3(CN)_{11}.H_2O$.	Found. I.	Found. II.
Carbon	16.40	16.84	16.83
Water	0.25	0.41	0.30
Cobalt	21.99	22.09	21.82
Silver	40.24	39.73	39.89

The silver salt is a salmon colored, flocculent precipitate, which turns brick-red when dried in the air, and becomes slate green *in vacuo*; but like all the other salts of this acid it takes up water again with the utmost ease, even a few seconds exposure to the air being enough to restore its red color.

Cupric Cobaltocobalticyanide, $Cu_3[Co_3(CN)_{11}]_2.4H_2O$.—This salt was made by precipitating a solution of the monopotassic salt with cupric sulphate. The greenish-blue, flocculent precipitate was washed thoroughly with water and then dried *in vacuo*. When dry and pulverized it formed a bright, emerald green powder.

0.2534 gram of the salt, dried *in vacuo*, gave 0.2080 gram of carbonic dioxide, 0.0246 gram of water, 0.1950 gram of cobaltous sulphate, and 0.0412 gram of copper.

	Calculated for $Cu_3[Co_3(CN)_{11}]_2.4H_2O$.	Found.
Carbon	22.22	22.39
Hydrogen	0.67	1.08
Cobalt	29.80	29.29
Copper	16.01	16.26

Zincic Cobaltocobalticyanide, $ZnHCo_3(CN)_{11}.3H_2O$.—This salt was made by adding to an alcoholic solution of the monopotassic salt an aqueous solution of zincic chloride; a salmon-

pink precipitate was thrown down which was washed with alcohol. This substance was analyzed with the results given under I. In a second experiment aqueous solutions were used and an exactly similar result was obtained, the analysis of which is given under II. For the first analysis the salt was dried at 100°, when it took on a grayish color; for the second it was dried *in vacuo*.

I. 0.3540 gram of the substance gave 0.2923 gram of carbonic dioxide, 0.0442 gram of water, and 0.0470 gram of zincic oxide.

II. 0.3865 gram of the substance gave 0.3253 gram of carbonic dioxide and 0.0374 gram of water.

	Calculated for $ZnHCo_3(CN)_{11}\cdot 3H_2O$.	Found. I.	II.
Carbon	22.64	22.52	22.94
Hydrogen	1.20	1.39	1.08
Zinc	11.15	10.65	....

The analysis of these salts prove conclusively that the acid is tribasic.

The free hydrocobaltocobalticyanic acid was obtained by treating hydrocobalticyanic acid with nitric acid precisely as was done with the potassic cobalticyanide in making the monopotassium salt. It resembles this salt most closely in its red color, gelatinous consistency, and solubility, but, is less stable, as it gives off hydrocyanic acid when dried. On this account we did not attempt to analyze it.

Action of Potassic Hydrate on Monopotassic Cobaltocobalticyanide.

When an excess of potassic hydrate was added to a solution of the monopotassic cobaltocobalticyanide, it turned dark-brown in the cold, and, if the liquid was warmed, this color deepened to a black, but nothing was precipitated until the solution was boiled, when after a few minutes a black precipitate of cobaltic hydrate was formed. The separation of this cobaltic hydrate is slow and gradual. It required from twenty-four to thirty-six hours to remove the whole of it. Before it is complete, if the precipitate was filtered out, a yellowish solution was obtained, from which renewed boiling separated more of the cobaltic hydrate. After no more cobal-

tic hydrate was formed the liquid was filtered and the light-yellow filtrate acidified with acetic acid, when no odor of hydrocyanic acid was observed. Alcohol was then added, which precipitated fine yellow or white needles, the excess of potassic hydrate, which had been converted into potassic acetate, remaining in solution. The precipitate was dissolved in a little water and then treated with an amount of alcohol insufficient for complete precipitation. This threw down a yellow oil, which was filtered out and the addition of an excess of alcohol to the filtrate gave a precipitate of white needles. The needles were purified by crystallization from water three times, and then analyzed with the following results:

I. 0.1620 gram of the substance, dried *in vacuo*, gave on combustion 0.1286 gram of carbonic dioxide.[1]

II. 0.3094 gram of the substance, dried at 100°, gave 0.1450 gram of cobaltous sulphate and 0.2438 gram of potassic sulphate.

	Calculated for $K_6Co_2(CN)_{12}$.	Found. I.	Found. II.
Carbon	21.67	21.65	....
Cobalt	17.75	....	17.84
Potassium	35.30	....	35.37

The substance is therefore, according to this analysis, potassic cobalticyanide, but we found it hard to believe this was the case, because it crystallized, as already stated, in little needles most unlike the characteristic broad, rhombic crystals of the potassic cobalticyanide, and we could not, even by numerous crystallizations, succeed in making it crystallize in the usual form. We decided, therefore, that some confirmatory work was necessary before we admitted that this substance was potassic cobalticyanide, and for this purpose converted it into the sodium salt, which crystallizes with water. The potassium salt was first converted into the copper salt, and this by sulphuretted hydrogen into the free acid. The copper salt had the color of the cobalticyanide and the acid crystallized in long silky needles exactly resembling those derived from a sample of ordi-

[1] In the combustion 0.0050 gram of water were found amounting to 0.34 per cent. It was undoubtedly hygroscopic.

nary potassic cobalticyanide, but on neutralizing a little of each of these preparations with potassic hydrate, the one from our salt gave needles, that from the ordinary cobalticyanide rhombic crystals as before. The main portion of each sample of acid was converted into the sodium salt by neutralization with sodic hydrate, each sample dried *in vacuo*, and the water of crystallization determined with the following results:

I. 0.3644 gram of the sodium salt prepared from the needle-formed potassium salt, lost 0.0442 gram when dried at 100°.

II. 0.5342 gram of the sodium salt prepared from potassic cobalticyanide lost 0.0626 gram when dried at 100°.

	Calculated for $Na_8Co_3(CN)_{12}.4H_2O$.	Found. I.	II.
Water	11.25	12.13	11.71

There can be no doubt therefore that the substance obtained by us through the action of potassic hydrate on potassic cobaltocobalticyanide is potassic cobalticyanide. We are inclined to think that the unusual crystalline form, in which it appeared, was due to the presence of a small amount of impurity, probably the oily product of the reaction already mentioned, although the analyses show that the needles were nearly pure potassic cobalticyanide, and in some experiments we found that it was necessary to add a very large amount of this oily impurity to potassic cobalticyanide to make it crystallize in needles; in fact the needles began to appear only when so much of the mixture of oil and our needle-formed cobalticyanide had been added, that they might have consisted of this, crystallizing out.

The secondary product, which was precipitated as an oil, was converted into a very deliquescent yellow solid by drying at 100°. We have not yet succeeded in finding a method of purifying it, but hope that some experiments now in progress may bring it into a state fit for analysis. When the triargentic cobaltocobalticyanide was treated with sulphuretted hydrogen, what seemed to be a new compound was formed, which will be investigated in this laboratory.

Conclusion.

Many of the peculiar properties of the substances described in this paper also appear in the ferrocyanides and ferricyanides. Thus Prussian blue is a colloid substance like our monopotassium salt, and the obstinacy with which our salts retain their water (the silver salt at 130°, the barium salt even at 180°), recalls the fact that Prussian blue dried at 100° contains, according to Carius and Reimann,[1] 12 molecules of water, and even when heated to 160°, according to Rammelsberg,[2] 9 molecules, which are not given off till 250°. The solubility of the monopotassium salt also is like that of soluble Prussian blue up to a certain point, since both are insoluble as at first formed, but become soluble when the impurities are washed out, and are rendered insoluble in cold water by drying at 100°, but we cannot find that the soluble Prussian blue shows the property of dissolving again in warm water, after it has been rendered insoluble in cold, which is so characteristic of our monopotassium salt.

This analogy between soluble Prussian blue and our monopotassium salt might lead to the supposition that they were similarly constituted, in other words that one of the atoms of cobalt in our compounds is in the basic part of the salt, but, if this were so, potassic hydrate should give a precipitate of cobaltous hydrate in the cold, and it does not. A precipitate is formed, to be sure, on boiling our monopotassium salt with potassic hydrate, but it is cobaltic hydrate, and is attended by a complete decomposition of our compound into potassic cobalticyanide and the salt of some other, as yet unrecognized acid. Further, on this supposition, the atom of basic cobalt should be replaced by two of silver, when the monopotassium salt is treated with argentic nitrate, but this is not the case, as the salt $KH_3Co_3(CN)_{11}$ gives under these conditions the triargentic salt $Ag_3Co_3(CN)_{11}$. We must infer, therefore, that all of the cobalt in our salts is in the acid part of the molecule.

None of the compounds of iron and cyanogen seem to be constituted like our salts, so that we cannot help ourselves

[1] Ann. Chem. (Liebig), **113**, 41. [2] Pogg. Ann., **73**, 80.

by analogy in speculations on the nature of these salts. In the absence of definite knowledge in regard to their constitution we have thought it wise to rest on the fact that the formula $H_3Co_3(CN)_{11}$ amounts to 3 molecules of hydrocyanic acid combined with one of cobaltocobalticyanide, thus $(HCN)_3Co_3(CN)_8$, and therefore to give these substances the provisional name of cobaltocobalticyanides.

We hope that the work will soon be extended in this laboratory to compounds analogous to the cobalticyanide. We have tried already some preliminary experiments on potassic ferricyanide, which was converted by boiling with nitric acid into a black jelly having similar properties to the red gelatinous monopotassic cobaltocobalticyanide, and drying to a jet black varnish. As it seemed less stable than the corresponding cobalt compound, we have postponed its study, until we have mastered that substance. Its black color recalls that of potassic perferricyanide, but it seems to be still more closely related to the black compound, $Fe_3(CN)_8$, which Edgar Reynolds[1] obtained by the action of bromine on potassic ferricyanide.

ON THE ANALOGIES IN COMPOSITION OF THE SALTS OF CALCIUM, STRONTIUM AND BARIUM.

By J. H. Kastle.

That certain analogies in the composition of calcium, strontium and barium salts, anhydrous and hydrated, exist has, of course, been recognized for a long time. In fact the resemblance in composition between the chlorides, nitrates, sulphates, etc., of these elements is nearly always cited as one of the strongest arguments in favor of the family relationship of these metals.

To what extent such analogies exist has, so far as I can discover, never been made out. It is true that along this line a great many attempts have been made to trace resemblances and find relationships existing between the hydrated salts of related acids and metals.

Important contributions to our knowledge of this subject

[1] J. Chem. Soc. (London), **53**, 767 (1888).

have been made by Salzer,[1] whose rules concerning water of crystallization are doubtless familiar to the majority of chemists. His work has, however, no immediate bearing upon the problem in hand, and hence will not be discussed. In fact the only work bearing immediately upon the subject under consideration is that of Lenssen.[2] As the result of his work on triads of related elements, this observer was led to conceive of a more intimate relation existing between two of the elements composing the triad than was supposed to exist between those composing the triad itself. In other words, he assumed the existence of a dyad within the triad. Among the other facts which he cited in support of his conclusion were the relationships existing between the amounts of water of crystallization of the salts of the two metals composing the dyad, and concerning which he laid down the following rules:

The salts which an acid forms with members of a dyad contain:

1. Equal numbers of molecules of water of crystallization, or are anhydrous respectively, or

2. That salt contains the greater number of molecules of water of crystallization whose base has the smaller equivalent in the dyad.

According to him calcium, strontium and barium form a triad in which the dyad relation is exhibited by strontium and barium; and in support of his theory he cited the composition of the strontium and barium salts of 30 acids; and, in the case of strontium and barium salts, he reached the further conclusion that the salts of these two metals either contain the same number of molecules of water of crystallization or the strontium salts contain 4 more than those of barium.

Without entering into a detailed criticism of Lenssen's conclusion, it may be observed that while the relations of elements as implied in the triad are still about the closest of those exhibited in the natural family, it would seem that the necessity for the still further and inner relation of the dyad within the triad itself has never made itself felt. It is, further, to be borne in mind that many valuable contributions to our knowledge of the chemistry of the salts of metals and

[1] Ann. Chem. (Liebig), **223**, 1. [2] *Ibid*, **103**, 121.

acids have been made since this time (1857), and that the data now at hand are vastly greater than they were then.

It was deemed advisable, therefore, to institute this comparison as to the composition of calcium, strontium and barium salts, anhydrous and hydrated,[1] and it will be seen that the analogies existing in the composition of the salts of these metals are deeper and more comprehensive than those included in Lenssen's rules.

The following standard works of reference were used in making this comparison: Watts' Dictionary of Chemistry, (Morley and Muir); Beilstein's Handbuch der organischen Chemie; Comey's Dictionary of Solubilities. The examination showed that 141 acids have been described, whose calcium, strontium and barium salts all have been prepared and studied.[2] In the case of 34 of these acids it was found that their calcium, strontium and barium salts are all three analogous in composition; *i. e.*, if the salt of one of these metals is anhydrous, so also are the salts of the other two. If one, say the calcium salt of any given acid contains 6 molecules of water of crystallization, then the corresponding strontium and barium salts are found to contain the same number. Secondly, in the case of 79 of these acids, the salts of two of these metals were observed to be analogous in composition; *i. e.*, either the calcium or strontium, or the calcium and barium, or the strontium and barium salts of a given acid resemble each other in the sense that, if the salt of either of these metals is anhydrous, so also is the salt of one of the others; or if one salt, say the calcium, contains a certain number of molecules of water of crystallization, then either the strontium or barium salt is found to contain the same number.

It is believed that these analogies in composition of calcium, strontium and barium salts are sufficiently numerous to warrant the following generalization:

[1] As stated above, this comparison includes the anhydrous as well as the hydrated forms of the salts of these metals. It is believed that the former should be included in any general consideration of these elements. It is certainly just as characteristic that barium should form an anhydrous sulphate as it is that its chloride contains two molecules of water of crystallization.

[2] It would require entirely too much space to give even abbreviated symbols representing the composition of these salts. The names of these acids will be found in Table I, p. 287, together with the list of exceptions on p. 284.

Of the calcium, strontium, and barium salts of any acid, all or two of the salts of these metals will be found to be analogous in composition.

In support of this conclusion there are, in the first place, the salts of 113 acids out of the 141, where calcium, strontium and barium salts have all been described, and whose analogies have already been discussed; in addition to which we have also the salts of 139 acids[1] of which the salts of only two of these metals have been described in the literature, which two salts, however, are analogous in composition.[2]

The salts of 252 acids out of 280, exhibit analogies in composition in conformity to the above rule. Among those acids, whose calcium, strontium and barium salts have all been described, numbering 141, there are 28 whose salts do not show their analogies.

These are:

Amidoisophthalic,	Ethylsuccinic,
Hippuric,	Dibrombenzoic,
Adipic,	Bromnitrobenzoic,

[1] Want of space prevents even giving the names of these 139 acids. If there are any who are especially interested in this line of work, I will be glad to supply them with this list of acids and such of their calcium, strontium and barium salts as have been described.

[2] It is somewhat surprising to find how very considerable is the number of acids described in the literature, of which no salt has been prepared at all. Again there are quite a number of acids, only one of whose salts is described, usually the silver or the barium; and again quite a considerable number of others of which salts of only two of the metals under consideration are described. Of these, the calcium and barium salts are the two most often described, though of course the calcium and strontium and the strontium and barium are sometimes given. As stated above, in the case of 139 acids, the only two salts of the metals of calcium family described are analogous in composition. In the case of probably the same number of acids, certainly not more, the only two salts of these metals which are described are not analogous in composition. This, however, does not show necessarily that the calcium, strontium and barium salts of these do not conform to the above rule. For example, in the case of a-β-dichloracrylic and β_1-dichloracrylic acids, only the calcium and barium salts have been prepared. In the case of β_1-dichloracrylic acid, the calcium and barium salt each contains 2 molecules of water of crystallization, hence β_1-dichloracrylic conforms to the rule. In the case of the a-β-dichloracrylic acid, however, the calcium salt contains 3 and the barium salt 1 molecule of water of crystallization; hence it might be argued that the salts of this acid show an exception to the rule. As a matter of fact this is simply one of those cases in which the data are too incomplete to justify any positive conclusion. The strontium salt yet remains to be prepared: it may happen, and in fact there are some grounds for believing that it will happen, that this salt will contain the same amount of water of crystallization as either the calcium or barium salt; or even two hydrates of it may be found to exist, one corresponding to the calcium, the other to the barium salt, when in either case the analogies would conform to the rule.

Chlornitrobenzoic,	Bromnitrotoluenesulphonic,
Retenedisulphonic,	Dimethylsuccinic,
Mesitylenesulphonic,	Nitroisophthalic,
u-Durenesulphonic,	Gallic,
Saccharic,	Isopimelic,
Dibrom-(*o*)-amidobenzoic,	Terephthalic,
αα-Dibrompropionic	Permanganic,
Trichlorbenzoic,	Dichromic,
Deconic,	Metatungstic,
Lactic,	Chlorplatinous,
Carboxyamidobenzoic,	Platiodonitrous.

Without in any way attempting to explain these exceptions, it is to be observed first that in the case of several of these acids there exist discrepancies in the literature in regard to the composition of their salts. This is true of four of the above acids, *viz.*, gallic, nitroisophthalic, dibrombenzoic and carboxyamidobenzoic. According to Watts' Dictionary the salts of these do not show the analogies under discussion; whereas, according to Beilstein, at least two of their salts are analogous. Plainly, therefore, these acids have to be omitted from the discussion until these discrepancies can be cleared up.

Secondly, it should be borne in mind, in this connection, that the acids, whose salts are under discussion, represent the greatest diversity in composition and properties; and the determination of the composition of their salts represents the work of a very large number of men. Such being the case, it would seem probable, at least, that quite a number of errors in the composition of these salts must of necessity have crept into the literature. This is rendered all the more probable in the case of hydrates, for the reason that, in these compounds the water of crystallization is often determined by difference.

Lastly, it should be remembered that in many instances, even in the case of many of the salts of the acids here under discussion, not only one or two, but even several perfectly distinct hydrates of the same salt have been obtained. In view of which, it can hardly seem far-fetched to suppose that as the result of future investigation, other hydrates of those calcium, strontium and barium salts now forming the above

exceptions, will be discovered of such a character as to exhibit the analogies in question.

There is another interesting feature of the results. This question naturally suggests itself regarding the resemblances which have been pointed out above, *viz.*, are these resemblances greater between the salts of calcium and strontium than between those of strontium and barium, or those of calcium and barium; or are these resemblances about equally distributed between the salts of these three metals? Or, in other words, do these metals also show themselves alike, or different in this respect, or do they exhibit something of a graduation of properties, so far as these analogies in the composition of their salts are concerned?

The arrangement of the acids, whose calcium, strontium and barium salts are described in the literature, as given in the following table, is intended to show whatever relation may exist in this regard.

Table No. I.

I. Acids whose calcium, strontium and barium salts are all analogous.	II. Acids whose calcium and strontium salts are analogous.
Aconitic,	Hydrochloric,
Diglycollic,	Salicylic,
Nitroamidobenzoic [3 : 2 : 1],	Anisic,
p-Nitrotoluene-(*o*)-sulphonic,	Nitric,
Amylmalonic,	Sulphocyanic,
Trichloracetic,	Citraconic,
Isoamylsulphonic,	Butyric,
Pyrotartaric,	Isobutyric,
Oxalic,	Glycollic,
Oxyazelaïc,	Iodic,
Ricinoleic,	*p*-Iodobenzoic,
Isosaccharic,	Cumene-(*α*)-sulphonic,
Sebacic,	Phenylglyoxylic,
Stearic,	Quinic,
Sulphuric,	Tartaric,
Uramidic,	Racemic,
Bromic,	Hydrobromic,
Triethylacetic,	Citric,
Fumaric,	Lauric,
Hydrofluoric,	Fluosilicic,
Molybdic,	Fluostannic,
Iodoauricyanhydric,	Hypophosphorous,
Nitrous,	Imidosulphonic,
Dithionic,	Tetraboric,
Plumbic,	Phosphorous,
Sulpharsenic,	Platinocyanic,
Dimesoperiodic,	Perbromplatinocyanhydric,
Orthoperiodic,	Perchloric,
Orthophosphoric,	Telluric,
Tellurous,	Tungstic,
Uranic,	Metavanadic,
Zirconic,	Chlorplatinic.
Carbonic,	
Chromic.	
Total 34	Total 32

Table No. I—Continued.

III. Acids whose calcium and barium salts are analogous.	IV. Acids whose strontium and barium salts are analogous.
Nitro-(*o*)-oxybenzoic,	Azelaïc,
p-Nitrocinnamic,	Nitric,
Citric,	Citric,
Isoheptylic,	(*m*)-Nitrobenzoic,
Ferrocyanic,	Alloxanic,
Formic,	(*m*)-Bromtoluenesulphonic,
Acetic,	(*p*)-Bromtoluenesulphonic,
(*p*-*N*)-Cuminic,	Caffeïc,
Chloracetic,	Carbamic,
Chloric,	Glyceric,
Ethylsulphuric,	*N*-Caproic,
Isoheptoïc,	Iodic,
(*γ*)-Chlorisophthalic,	(*β*)-Chlorethanesulphonic,
Propionic,	(*p*)-Diethylbenzenesulphonic,
Maleïc,	Polyporic,
Malonic,	Prypionic,
Tolylene (*m*)diaminesulphonic	Selenic,
Propionic,	Suberic,
Citraconic,	Succinic,
Arsenious,	Sulphurous,
Malic,	Sulphopropionic,
Chlorstannic,	Thiosulphuric,
α-Bromacrylic,	Methanesulphonic,
Metaboric,	*α*-Oxy-(*α*)-methylglutaric,
Hydrocyanic.	Isovaleric,
	Propionic,
	Arsenic,
	Arsenious,
	Orthophosphoric (in acid salts),
	Zincic.
Total 25	Total 30

From this table it can be seen at a glance that of the 113 acids included therein, there are 34 whose calcium, strontium, and barium salts are all analogous in composition. In the case of trichloracetic acid, for example, the calcium, strontium, and barium salt each crystallizes with 6 molecules of water of crystallization. Secondly, there are 32 acids whose calcium and strontium salts are analogous in composition, 25 in which the analogy has been found to exist between the calcium and

barium salts, and 30 in which it exists between the salts of strontium and barium. It will be observed that, in several instances, the same acid, for example, nitric acid, appears in two columns of the above table. This is for the reason that double or even triple analogies are sometimes displayed among the calcium, strontium, and barium salts of the same acid. In the case of nitric acid, the calcium salt crystallizes with 4 molecules of water; the strontium salt may be obtained either as an anhydrous salt or with 4 molecules of water; the barium salt is anhydrous.

Hence a double analogy exists here, one between the strontium and barium salts, both of which are anhydrous; and one between the calcium and strontium salts, both of which contain 4 molecules of water of crystallization.

The results of the comparison, as set forth in the above table, would certainly seem to show that the analogy in question is about equally distributed between calcium, strontium and barium; or, in other words, that the analogy in composition of the calcium, strontium and barium salts of any given acid is just as likely to show itself between the salts of all three of these metals, or between the calcium and strontium salts of that acid, as it is between the calcium and barium salts, or those of strontium and barium, and *vice versa;* or that, so far as composition of their salts is concerned, these three metals are altogether similar.

All this of course is opposed to the conclusions of Lenssen, to which reference was made at the beginning of this paper, and according to which strontium and barium are so closely similar in general properties and show such close analogies in the composition of their salts with various acids, as to compose a closely related group or dyad within the calcium, strontium and barium group or triad itself.

In conclusion it may be said that it can hardly be the result of chance or coincidence that out of 280 acids of the most widely different composition and properties, we have 252 in which are exhibited these striking analogies and relationships in the composition of their calcium, strontium, and barium salts. As has been indicated elsewhere in this paper, our knowledge of even the salts of so small a group of metals as

the alkaline earths, is still far from complete; and hence it would seem inevitable that new relations as to the composition of salts of nearly related metals will sometime be discovered; and therefore it may well be that, in such cases as that furnished by the calcium, strontium, and barium salts of mesitylenesulphonic acid; $CaA_2.5H_2O$; $SrA_2.7H_2O$; $BaA_2.9H_2O$, which now form an exception to our rule of analogies, we are in reality catching glimpses of another relationship between the salts of these metals as important and characteristic as that under consideration. It is believed, however, that the considerations advanced in the above are in keeping with the facts as they are known to us at present.

In conclusion I desire to thank Mr. Jos. Frazer, Mr. W. A. Beatty, and Miss Logan H. Warner for their very kind assistance in the arrangement and compilation of the data herein discussed.

STATE COLLEGE OF KENTUCKY,
LEXINGTON, DECEMBER, 1896.

Contributions from the Chemical Laboratory of the University of Illinois.

ACTION OF MERCAPTIDES ON QUINONES.

BY H. S. GRINDLEY AND J. L. SAMMIS.

(Preliminary Notice.)

A few years ago Professor C. Loring Jackson and one of us[1] found that quinones, when treated with alcoholates, give compounds which belong to the class of acetals. It was proved that these substances are formed by the addition of 2 molecules of alcohol to the two carbonyl groups of the quinone. They were named by us *hemiacetals*. In this connection it was thought that the study of the action of mercaptides on quinones would be of value and of interest. The following paper contains a description of the results thus far obtained in this direction:

The action of sodium mercaptide on dichlordiphenoxyquinone was first studied, and we found that if the substances were mixed in dry ether in the proportion of 6 molecules of the former to one of the latter, a yellow crystalline salt was formed which was insoluble in the ether, but soluble in water. It was un-

[1] This JOURNAL, 17, 577.

stable, being decomposed immediately when exposed to the air. It also decomposes readily in the presence of water, forming the product tetrathioethylquinone, $C_6(S.C_2H_5)_4O_2$, which melts at 90°–91°, and gives a hydroquinone melting at 58° when treated with reducing agents.

The tetrathioethylquinone, when treated with two equivalents of sodium mercaptide, gives the yellow crystalline salt which was formed above by treating dichlordiphenoxyquinone with 6 equivalents of the mercaptide. This substance is so unstable that so far we have not been able to prepare it pure enough for analysis, but the method of formation and the properties of this salt indicate that it is similar in structure and belongs to the same class of compounds as those obtained by Jackson and Grindley, by treating substituted quinones with alcoholates. The sodium salt, when treated with benzoyl chloride in alcohol solution, gives the compound tetrathioethylquinone-dibenzoyldithiobenzoylacetal,

$$C_6(S.C_2H_5)_4(O.CO.C_6H_5)_2(S.CO.C_6H_5)_2.$$

This substance, when treated with zinc dust and glacial acetic acid, remains unchanged. It is not affected by hydroxylamine hydrochloride.

Action of Sodium Mercaptide on Dichlordiphenoxyquinone.—In order to study this action 5 grams of dichlordiphenoxyquinone suspended in ether, were treated with sodium ethyl mercaptide, which was made by dissolving 1.95 grams of metallic sodium in 10 grams of ethyl mercaptan dissolved in about 20 cc. of pure dry ether. This gave the proportion of 6 molecules of sodium mercaptide to 1 of dichlordiphenoxyquinone. When the two substances were brought together the reaction began at once, and heat was produced, the red dichlordiphenoxyquinone being changed into a yellow crystalline substance. In order to complete the reaction, the mixture was heated on the water-bath for a few minutes. The ether solution was rapidly filtered, and the precipitate washed with ether. The yellow substance, while still moist with ether, was put into water. It dissolved at first, giving a clear solution, but on standing a short time the aqueous solution underwent a decomposition, a green crystalline body separating.

This decomposition in water takes place slowly and seems to be assisted by exposing the aqueous solution to the action of the air. The decomposition-product was filtered off and, after washing with water, was purified by recrystallization from hot alcohol until it showed the constant melting-point of 91°. The analysis of the substance dried over sulphuric acid for several days gave the following results:

I. 0.2061 gram substance gave on combustion 0.3680 gram CO_2 and 0.1145 gram H_2O.

II. 0.2203 gram substance gave on combustion 0.3932 gram CO_2 and 0.1200 gram H_2O.

III. 0.1199 gram substance gave, on fusion with sodium carbonate and potassium nitrate, 0.3207 gram $BaSO_4$.

IV. 0.1892 gram substance gave on fusion with sodium carbonate and potassium nitrate, 0.5069 gram $BaSO_4$.

	Calculated for $C_6(S.C_2H_5)_4O_2$.	Found. I.	II.	III.	IV.
C	48.27	48.67	48.67	....	....
H	5.75	6.17	6.05	....	....
S	36.78	....	....	36.72	36.80

From these results it is evident that the substance is tetrathioethylquinone. This same product is also formed by treating chloranil with sodium mercaptide. The yield is very small in both cases.

Properties of Tetrathioethylquinone, $C_6(S.C_2H_5)_4O_2$.— The substance crystallizes from alcohol in beautiful glossy, dark-green needles. It melts at 90°–91°. It is readily soluble in chloroform, benzol, glacial acetic acid, and carbon disulphide; soluble in ethyl alcohol, methyl alcohol, ligroïn, and ether. It is insoluble in water, either cold or hot. Tetrathioethylquinone is soluble in strong sulphuric acid, but is precipitated from the solution unchanged on the addition of water. It is insoluble in cold or warm concentrated hydrochloric acid. It is soluble in concentrated nitric acid with the evolution of oxides of nitrogen. It imparts a beautiful red coloration to the acid and is not reprecipitated on the addition of water. The nature of this reaction will be studied in this laboratory at an early date. It is easily reduced to the corresponding

hydroquinone by the action of glacial acetic acid and zinc dust.

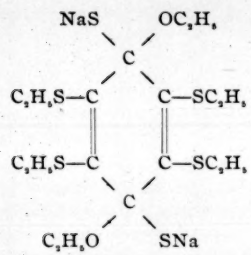
Tetrathioethylhydroquinone, $C_6(S.C_2H_5)_4O_2H_2$.—This substance was made by reducing the tetrathioethylquinone with glacial acetic acid and zinc dust. Three grams of the tetrathioethylquinone were warmed on the water-bath with these reagents until the dark-green color of the original had completely disappeared. Water was then added, and the precipitated hydroquinone was purified by recrystallizing it from alcohol containing a little hydrochloric acid to prevent oxidation. On analysis the following result was obtained :

0.24935 gram substance gave on fusion with sodium carbonate and potassium nitrate 0.6619 gram $BaSO_4$.

	Calculated for $C_6(SC_2H_5)_4(OH)_2$.	Found.
S	36.57	36.46

Properties of Tetrathioethylhydroquinone. — It crystallizes from alcohol in large colorless prisms, which melt at 58°–59°. It is insoluble in water; soluble in ligroïn, methyl alcohol, or ethyl alcohol; readily soluble in glacial acetic acid, benzol, or ether; very readily soluble in chloroform. The tetrathioethylhydroquinone dissolves in concentrated sulphuric acid, giving the acid a light-green color. It dissolves in concentrated nitric acid with effervescence, giving the solution a bright-red color. The addition of water does not cause the separation of anything. Concentrated hydrochloric acid has no effect upon the hydroquinone.

Tetrathioethylquinonedibenzoyldithiobenzoylacetal, $C_6(S.C_2H_5)_4(O.CO.C_6H_5)_2(S.CO.C_6H_5)_2$.—This substance was prepared from the yellow crystalline salt of sodium obtained as described above by the action of sodium mercaptide on tetrathioethylquinone. The method of formation and the properties of this salt are so similar to the salts of the hemiacetals of quinone obtained by Jackson and Grindley that for the time we have assumed it to have an analogous constitution which would be represented by the following structural formula :



It is then the sodium salt of tetrathioethylquinone-dithioethylhemiacetal. This salt is so very unstable that so far we have not succeeded in getting it pure enough for analysis. However, we hope by further study to obtain this salt sufficiently pure to make determinations of the amount of sodium present.

The tetrathioethylquinonedibenzoyldithiobenzoylacetal was obtained by treating the above sodium salt (which was prepared in ether and kept covered with a layer of the same to prevent decomposition) with benzoyl chloride. Action took place readily, the yellow salt going into solution and sodium chloride separating. After the action was complete the ether was removed by evaporation and the residue was treated with a dilute solution of sodium carbonate to remove the benzoic acid formed. After this treatment there was left a semi-liquid residue, which on treatment with alcohol immediately became a crystalline solid. This solid was recrystallized from alcohol until it showed a constant melting-point of 131°–132°. The analysis of the substance, dried at 100°, gave the following results:

I. 0.2123 gram substance gave on combustion 0.4718 gram CO_2 and 0.11085 gram H_2O.

II. 0.2267 gram substance gave on combustion 0.5050 gram CO_2 and 0.1075 gram H_2O.

III. 0.2238 gram substance gave on fusion with Na_2CO_3 and KNO_3, 0.37255 gram $BaSO_4$.

IV. 0.11514 gram substance gave, on fusion with Na_2CO_3 and KNO_3, 0.19215 gram $BaSO_4$.

	Calculated for $C_6(S.C_7H_5)_4(O.CO.C_6H_5)_2(S\cdot CO.C_6H_5)_2$. I.	Found. II.	III.	IV.
C	60.57	60.60	60.74	....	....
H	4.81	5.80	5.26	....	....
S	23.07	....	....	22.88	22.92

The analysis of this substance was very difficult, owing to the high percentage of sulphur, and the high percentages of hydrogen found were undoubtedly due to this cause.

Properties of Tetrathioethylquinonedibenzoyldithiobenzoylacetal.—It crystallizes from alcohol in two distinct forms, which are easily changed from the one to the other. When the solution is concentrated and cooled quickly the crystals form as long slender prisms. When the alcoholic solution is not so concentrated and is cooled slowly the crystals form as rhombic plates. It melts at 131°–132° and is readily soluble in benzol, chloroform, or ether; soluble in ethyl alcohol, methyl alcohol, or glacial acetic acid. It is insoluble in water or ligroïn.

The study of the action of mercaptides on quinones will be continued in this laboratory.

URBANA, ILL., Jan. 24, 1897.

Contribution from the Kent Chemical Laboratory of the University of Chicago.

THE ACTION OF SODIUM ETHYLATE ON AMIDE BROMIDES.

BY S. E. SWARTZ.

In 1881–2 A. W. Hofmann[1] developed a method for the formation of amines from acid amide bromides by treatment with caustic alkali, and proved that, in the course of the reaction, an isocyanate is first formed, which, by treatment with silver carbonate, he was able to isolate:

$$2C_2H_3ONHBr + Ag_2CO_3 = CH_3NCO + 2AgBr + H_2O + CO_2.$$

Hoogewerf and Van Dorp[2] improved the conditions of the reaction by using potassium hypobromite, and pointed out that the peculiar rearrangement which takes place in the molecule is perfectly analogous to the so-called Beckmann's rearrangement of ketoximes:

[1] Ber. d. chem. Ges., **14**, 2725; **15**, 407, 725, 762. [2] Rec. Trav. Chim., **9**, 33; **10**, 4.

$$\begin{array}{l} R-C-R \\ \quad\| \\ X-N \end{array} \rightarrow \begin{array}{l} X-C-R \\ \quad\| \\ R-N \end{array} ;$$

so also

$$\begin{array}{l} R-C=O \\ \quad| \\ Br-N-H \end{array} \rightarrow \begin{array}{l} Br-C=O \\ \quad| \\ R-N-H. \end{array}$$

The resulting bromformamides lose hydrobromic acid when treated with silver carbonate; with potassic hydrate they yield potassic carbonates (RNHCOOK), which Hoogewerf and Van Dorp were able to isolate in many cases, and which by saponification or treatment with acids yield amines. In the presence of an acid amide, the isocyanate or bromformamide unites with it, forming an acyl urea. For instance, acetamide bromide with potassic hydrate and acetamide gives as a final product acetyl methylurea.[1]

$$CH_3CONHBr + KOH + CH_3CONH_2 = \begin{matrix} CH_3HN \\ CH_3COHN \end{matrix}\!>\!CO + KBr + H_2O.$$

Lengfeld and Stieglitz have shown that when paranitrobenzamide bromide[2] or succinimide bromide is acted upon by sodium methylate, a similar arrangement is effected, giving urethanes by the action of methyl alcohol on isocyanates.

Work done in this laboratory by Mr. O. K. Folin[3] has shown, that, in general, when other amide bromides are treated with sodium methylate in methyl alcohol solution an analogous change takes place.

$$RCONHBr + CH_3OH = BrCONHR + NaOCH_3 = CH_3O.CO.NHR + NaBr.$$

In no instance has the bromine been directly replaced by the oxymethyl group.

Since molecular rearrangement of acid amide bromides is effected by a methyl alcohol solution of sodium methylate as well as by an aqueous solution of sodium hydroxide, and since, in these solutions, these substances not only exist as such but also are, to a greater or less extent, ionized, it was thought not impossible that by diminishing the electrolytic

[1] Ber. d. chem. Ges., **14**, 2725. [2] This JOURNAL, **15**, 215; 504, **16**, 307.
[3] The results will be published in the next number of this JOURNAL.—ED.

dissociation the rearrangement might be prevented and direct substitution effected.

At the suggestion of Drs. Lengfeld and Stieglitz the study of this question was undertaken by me. Dry succinimide bromide was treated with dry sodium methylate with and without a diluent, and, since ethyl alcohol causes a far smaller degree of electrolytic dissociation than methyl alcohol, various amide bromides which were found to suffer rearrangement in methyl alcohol were treated with a solution of sodium ethylate in ethyl alcohol.

It was found that succinimide bromide, treated with dry sodium methylate, regenerated succinimide, that no rearrangement took place, and that, at the same time bromine was not replaced by the methoxy group (CH_3O), but that the imido bromide was saponified or reduced, regenerating succinimide: with sodium ethylate in ethyl alcohol, in every case rearrangement was effected, and in no instance was any derivative of hydroxylamine obtained. The results obtained were perfectly analogous to those of Lengfeld and Stieglitz, and O. K. Folin, by the action of sodium methylate in methyl alcohol.

Experimental Part.

I. *The Action of Dry Sodium Methylate on Succinimide Bromide.*

Succinimide bromide, prepared according to the method described by Lengfeld and Stieglitz,[1] was dried for six days on clay plates over sulphuric acid in a vacuum desiccator, and the substance then carefully pulverized in a dry mortar. Sodium methylate was prepared immediately before using from absolute methyl alcohol, and was freed from alcohol in the usual way. The benzene was dried over sodium for four days and distilled.

Five grams of succinimide bromide and 1.6 grams of sodium methylate with 25 cc. benzene were heated in a sealed tube at 100° for two hours. On opening the tube a considerable quantity of gas escaped. The tube contained a dark red liquid, in which the odor of pyrrol was strong, and some un-

[1] This Journal, 15, 217.

dissolved material. The solution was neutral. Testing a portion with a hydrochloric acid solution of potassium iodide, there was no coloration, which indicated that no unchanged imide bromide remained. The contents of the tube were then extracted with hot benzene from which, on cooling, crystals were obtained which from their crystal form, solubility, and melting-point (125°) were identified as succinimide. The mother-liquor was then evaporated to dryness, and taken up with ether, and the colored solution digested with bone-black when the color disappeared. Ligroïn now precipitated more succinimide, and on distilling the ligroïn-ether solution a slight residue of almost pure succinimide remained. Washing the residue, insoluble in hot benzene, with water, there was obtained on evaporation the theoretical quantity of sodium bromide. While there remained insoluble in water and hot alcohol a tarry mass which amounted to almost 50 per cent. of the organic matter engaged in the reaction.

When 10 grams of succinimide bromide and 3.2 grams of sodium methylate in 100 cc. of benzene were heated under a reversed condenser the reaction was complete in four hours, no succinimide bromide remaining. The solution, which was a dark red, had a strong odor of pyrrol. Treated as above, it was found to contain about 70 per cent. of the theoretical amount of succinimide, and considerable tar, but no urethane or substituted hydroxylamine.

An attempt was made to study the effect of sodium methylate without a diluent on succinimide bromide, but the result was far from satisfactory, for when molecular quantities of the methylate and imide bromide were shaken together the action was explosively violent. When the imide bromide was added in small quantities, chemical change took place with somewhat less violence but was still very energetic. There resulted a black semi-charred mass with the odor of pyrrol, which, treated as above, yielded succinimide amounting to about 20 per cent. of the theoretical quantity, but no other organic substances could be isolated.

II. *The Action of Sodium Ethylate on Benzamide Bromide.*

To a solution of sodium ethylate prepared from 1.5 grams of

sodium in 60 grams of absolute ethyl alcohol, cooled in ice water, 12.8 grams of well dried benzamide bromide were added. Reaction began slowly, as was indicated by a gradual rise in temperature. Heated on a water-bath connected with a reversed condenser, well dried and closed with a calcium chloride tube, the solution became brownish red, and after twenty minutes, a test with acidulated potassic iodide showed that the action was complete. On cooling, a heavy precipitate appeared. The slightly alkaline solution was acidulated with a few drops of dilute acid, and then filtered. Washing the precipitate with cold water to remove the sodium bromide, and recrystallizing from hot alcohol, a substance was obtained in long white needles, melting at 199°. Subjected to dry distillation, the substance gave phenyl isocyanate, which was recognized by its odor, and benzamide (melting-point 128°). These decomposition-products, the melting-point 199°, the crystal form and solubility, together with the analysis, identify it as phenyl benzoyl urea described by Kühn.[1]

On analysis 0.2078 gram gave 21.6 cc. nitrogen at 18° and 742 mm. pressure.

	Calculated for $C_{14}H_{12}N_2O_2$.	Found.
Nitrogen	11.66	11.77

The alcoholic solution was evaporated to dryness on the water-bath and the solid residue extracted with chloroform, and dried over calcium chloride. The oil which remained was distilled under a pressure of 14–24 mm. It separated into two fractions which came over between 90°–120° and 140°–160°. The first fraction was a liquid which had a strong odor of phenyl isocyanate, and crystallized with difficulty, after standing four days. This was dried on clay plates and recrystallized from ligroïn, when a constant melting-point of 52° was obtained. This, together with its boiling-point, 238°, (750 mm.), identified the product as phenylurethane.

The higher fraction was a solid with a strong odor of benzonitrile. Recrystallizing from hot benzene, crystals were obtained which proved to be benzamide (melting-point 128°).

[1] Ber. d. chem. Ges., **17**, 2881.

Evidently some phenyl benzoylurea remained with the oil, and on distillation it decomposed, yielding phenyl isocyanate, obtained with the urethane, and benzamide, which in turn, gave a little benzonitrile.

The yield was: Phenyl benzoylurea, 53 per cent.; phenylurethane, 15 per cent.; benzamide, 18 per cent. of the theoretical.

Repetition of the experiment varying the conditions of temperature and concentration of the alcoholic solution resulted in only a slight variation in the relative amounts of the products.

Sodium ethylate in alcoholic solution evidently acts in two ways on benzamide bromide. On the one hand, it causes a rearrangement of a part of the benzamide bromide to bromformanilide in the manner indicated above:

$$1.\ C_6H_5CONHBr \rightarrow BrCONHC_6H_5.$$

On the other hand, it reduces the benzamide bromide to benzamide, since the odor of acetaldehyde was very prominent during the reaction:

$$2.\ C_6H_5CONHBr + NaOC_2H_5 = C_6H_5CONH_2 + NaBr + CH_3CHO.$$

The bromformamide then unites to a large extent with the benzamide, forming phenyl benzoyl urea:[1]

$$3.\ C_6H_5NHCOBr + C_6H_5CONH_2 = C_6H_5NHCONHCOC_6H_5 + HBr.$$

and to some extent with sodium ethylate still present, giving phenyl urethane:

$$4.\ C_6H_5NHCOBr + NaOC_2H_5 = C_6H_5NHCO_2C_2H_5.$$

From the yield it was found that 45–55 per cent. of the benzamide bromide had suffered rearrangement, giving phenyl benzoyl urea and phenyl urethane.

III. *The Action of Sodium Ethylate on Paranitrobenzamide Bromide.*

Paranitrobenzamide bromide, prepared after the method of Hoogewerf and Van Dorp, is very difficult to wash and dry,

[1] Ber. d. chem. Ges., 14, 2725.

and as potassium hydrate or water even in minute quantities furthers ionization, great care was taken to wash out all the caustic potash. The substance was then put on clay plates and dried in the open air for 24 hours, then pulverized and dried for six days in a vacuum-desiccator over sulphuric acid.

To a well cooled solution of one gram of sodium in 100 grams of absolute alcohol, 10.5 grams of *p*-nitrobenzamide bromide were added. Reaction began slowly at the temperature of the room, and heat was necessary to complete the change. After heating on a water-bath for twenty minutes, the contents of the flask needed only a drop of dilute acetic acid to render it slightly acid. Distilling off the alcohol and extracting the residue with absolute ether, a slightly yellow solution was obtained, which on cooling in a freezing-mixture, readily yielded a precipitate of yellow needles, which, after recrystallization from ligroïn, melted at 128°. This corresponded with paranitrophenyl urethane, prepared by Häger.[1] To identify the product more definitely, the urethane was prepared synthetically from chlorcarbonic ether and paranitraniline. It proved to be identical in color, crystal form, solubility and melting-point, with the body above described.

The action of sodium ethylate in alcoholic solution on paranitrobenzamide bromide, causes a rearrangement, yielding a urethane similar to that produced when it reacts with benzamide bromide:

1. $NO_2C_6H_4CONHBr + NaOC_2H_5 = NO_2C_6H_4NHCOBr + NaOC_2H_5$.

2. $NO_2C_6H_4NHCOBr + NaOC_2H_5 = NO_2C_6H_4NHCO_2C_2H_5 + NaBr$.

The residue left after extracting with ether was washed to remove the sodium bromide, and the remaining solid dissolved in hot alcohol. On cooling, a reddish brown precipitate was obtained, which after several precipitations, melted at 256°. The crystals are fine needles with a distinct yellow color, insoluble in cold alcohol, ether, ligroïn, chloroform, and acetone, and slightly soluble in hot alcohol.

The method of formation suggested, and the analysis proved,

[1] Ber. d. chem. Ges., 17, 2625.

this to be symmetrical paranitrophenyl-paranitrobenzoyl urea.

On analysis 0.1203 gram gave 18.8 cc. nitrogen at 742 mm. and 23°.

	Calculated for $C_{14}H_{10}N_4O_6$.	Found.
Nitrogen	16.98	17.16

It is formed according to the following reactions:

1. $NO_2C_6H_4CONHBr + NaOC_2H_5 = NO_2C_6H_4NHCOBr + NaOC_2H_5$.
2. $NO_2C_6H_4NHCOBr + NaOC_2H_5 = NO_2C_6H_4CONH_2 + NaBr + CH_3CHO$.
3. $NO_2C_6H_4NHCOBr + NO_2C_6H_4CONH_2 = NO_2C_6H_4NHCONHCOC_6H_4NO_2 + HBr$.

On adding water to the alcoholic solution from which *p*-nitrophenyl-*p*-nitrobenzoyl urea had been separated, crystals were obtained, which were found to be paranitrobenzamide.

The yield was: urethane, 20 per cent.; amide, 60 per cent.; urea, 15 per cent.

In greater concentrations (40 grams of absolute alcohol and 1 gram of sodium) no urea was obtained, but a higher per cent. of urethane (30–40), and a lower per cent. of the amide (50–55) resulted. One gram of sodium in 75 grams absolute alcohol gave analogous results. Yield: urethane, 30 per cent.; amide, 55 per cent.; urea, 10 per cent.

These results show that sodium ethylate in alcoholic solution acts in a perfectly analogous manner upon benzamide bromide and paranitrobenzamide bromide.

IV. *The Action of Sodium Ethylate on Orthonitrobenzamide Bromide.*

Orthonitrobenzamide bromide was prepared in the same manner as the corresponding para compound, 10.5 grams being added to a solution of one gram of sodium in 40 grams of absolute alcohol carefully cooled. The liquid turned slightly red, and part of the bromide went into solution, but it was necessary to heat on the water-bath to complete the reaction, but for a shorter time than in the case of paranitro-

benzamide bromide. At the end of seven minutes the amide bromide had completely disappeared. Acidifying with two drops of dilute acetic acid and cooling, a yellow precipitate was obtained. The alcoholic solution was evaporated to dryness and the residue, together with the precipitate was washed with cold water to remove the sodium bromide. After drying on clay plates, and extracting with ether, ligroïn precipitated from the solution an almost white crystalline body, which melted at 212°. Concentrating the ether-ligroïn solution, and cooling in a freezing-mixture, sulphur yellow crystals were obtained, which dissolved quite readily in warm ligroïn (boiling-point 40°–60°), and were again precipitated on cooling. These melted at 58°, and appeared to be identical with orthonitrophenyl urethane obtained by Rudolph.[1]

To identify it more fully the carbamic ester was synthetically prepared from orthonitraniline and chlorcarbonic ether. The two substances were identical.

The crystals melting at 212°, together with the residue left after extracting with ether, were digested with boiling ether. After filtering, the cooled filtrate gave an almost white precipitate which, crystallized from acetone, melted at 220°. This substance is difficultly soluble in ether, acetone, benzene and chloroform, but it dissolves readily in hot alcohol from which it is precipitated with difficulty on cooling, but the addition of water causes it to separate out very readily.

The method of formation and analysis show this to be orthonitrophenylorthonitrobenzoyl urea, $\begin{matrix} NO_2C_6H_4HN \\ NO_2C_6H_4CONH \end{matrix} > CO$.

On analysis 0.2037 gram gave 32 cc. nitrogen at 25° and 741 mm.

	Calculated for $C_{14}H_{10}N_4O_5$.	Found.
Nitrogen	16.98	17.13

To identify this body more fully, it was synthetically prepared by adding to an ethereal solution of orthonitrophenyl isocyanate the theoretical quantity of orthonitrobenzamide, which immediately yielded a precipitate identical with the above described urea:

[1] Ber. d. chem. Ges., 12, 1295.

$$NO_2C_6H_4NCO+NO_2C_6H_4CONH_2=\frac{NO_2C_6H_4NH}{NO_2C_6H_4CONH}>CO.$$

From the residue left after digesting with boiling ether, a small amount of orthonitrobenzamide was obtained by extracting with hot alcohol and precipitating by adding water. The yield from the reaction was as follows: urethane, 20 per cent.; urea, 60 per cent.; amide, 10 per cent.

A change in concentration of the alcoholic solution modified the relative amounts of the products to a slight extent, but gave no new substances.

One gram of sodium in 50 grams of absolute alcohol, with a molecular quantity of the amide bromide yielded of urethane, 30 per cent.; of urea, 50 per cent.; of amide, 10 per cent.

Change in conditions of temperature did not effect the results to any great degree.

IV. *The Action of Sodium Ethylate on Metanitrobenzamide Bromide.*

Metanitrobenzamide bromide was prepared in the same manner as paranitrobenzamide bromide. 10.5 grams of it were added to 1 gram of sodium in 100 grams of absolute alcohol. Chemical change took place more slowly than in the case of orthonitrobenzamide bromide, since no heat was manifested, and a longer time, 20 minutes, of heating on the water-bath was required to decompose the amide bromide.

During the reaction the odor of acetaldehyde was very strong. The slightly alkaline solution was acidified by a few drops of acetic acid, and freed from alcohol by heating on the water-bath. The residue was extracted with chloroform. From the chloroform solution, ligroïn precipitated metanitrobenzamide (melting-point 141°).

Distilling off the chloroform and ligroïn and taking up the residue with ether, ligroïn precipitated yellow needles which dissolved readily in low-boiling ligroïn (30°–40°), and were precipitated again on cooling in a freezing-mixture. These melted at 65°.

The method of formation indicated that this was metanitrophenyl urethane. To identify it more fully the carbamate was

synthetically prepared from metanitraniline and chlorcarbonic ether, and the product thus obtained proved to be identical with that crystallized from ligroïn. Analysis gave the following results:

0.1772 gram gave 21.6 cc. nitrogen at 20° and 743 mm.

	Calculated for $C_9H_{10}N_2O_4$.	Found.
Nitrogen	13.33	13.5

Metanitrophenyl urethane is a yellow substance which crystallizes in fine needles from ligroïn. It is readily soluble in ether, alcohol, chloroform, benzene and acetone. In ligroïn it dissolves more readily than the corresponding ortho or para compounds. It is almost insoluble in water. In alkalies it dissolves with difficulty with slight coloration. Heated in dilute alkalies it saponifies, yielding metanitraniline.

The yield was: urethane, 10 per cent.; amide, 80–90 per cent.

A change in the concentration of the alcoholic solution effected a change in both the relative quantities and the kind of products.

1. In quite dilute solutions, 1 gram of sodium in 300 grams of absolute alcohol and 10.5 grams of metanitrobenzamide bromide, the reaction was complete in 15 minutes when heated on the water-bath. The solution was strongly alkaline, and, on adding dilute acetic acid to neutralize, considerable carbon dioxide was given off. On allowing the solution to stand, an almost white crystalline body appeared, which melted at 230° and was identical with metanitrophenylmetanitrobenzoyl urea prepared by O. K. Folin[1] from metanitrophenyl isocyanate and benzamide.

When the alcohol was driven off from the filtrate from which the urea had been obtained, the residue was extracted with ether. From this solution ligroïn precipitated a mixture of metanitrobenzamide and metanitraniline. These were separated by dissolving out the nitraniline with ether in which the amide is very difficultly soluble. The amide was identified by its melting-point, 141°.2, its solubility and general appearance. The metanitraniline melted at 109°. In chloro-

[1] See note, p. 296.

form solution with dry hydrochloric acid it formed the hydrochloride.

Concentrating the ether-ligroïn solution from which nitraniline and nitrobenzamide had been obtained and cooling to —17° yellow crystals were obtained which melted at 65°, and were identical with the metanitrophenyl urethane previously obtained.

The yield was: urethane, 6 per cent.; amide, 15 per cent.; nitraniline, 55 per cent.; urea, 15 per cent.

2. In very dilute solutions, 1 gram of sodium in 600 grams absolute alcohol, and 10.5 grams of metanitrobenzamide bromide, treated in the same manner as above, no urea was obtained, but other products in the following proportion: Urethane, 6 per cent.; amide, 30 per cent.; nitraniline, 60 per cent.

3. In somewhat concentrated solution, 1 gram of sodium in 60 grams of alcohol there resulted 6 per cent. of urethane and 80–90 per cent. of the amide, and a small quantity of tar. No urea or nitraniline could be found.

4. In more concentrated solutions, 1 gram of sodium in 18 grams of alcohol, the yield was: urethane, traces; amide, 80–90 per cent.; tar, 5–10 per cent.

5. To study the effect of the presence of water when the amide bromide is treated with sodium ethylate, one gram of sodium was added to 60 grams of 98.5 per cent. alcohol, and to the cooled solution were added 10.5 grams of metanitrobenzamide bromide. No more heat was manifested than when the same concentration of absolute alcohol solution was used. The liquid became wine red on heating twenty minutes on the water-bath, when a portion tested with acidified potassium iodide, showed the presence of unchanged amide bromide. The substance then stood in the flask at the temperature of the room over night, when the action was found to be complete. In the flask was found a precipitate of metanitrophenylmetanitrobenzoyl urea. In the filtrate the urethane and amide were found but no nitraniline. The yield was as follows: Urethane, 5–7 per cent.; amide, 25–35 per cent.; urea, 40–50 per cent.

6. In 60 grams of 75 per cent. alcohol the same amounts of

amide bromide and sodium ethylate gave only the amide, 80–90 per cent., and tar.

It is evident that the course of the reaction is in principle analogous to that described as taking place when sodium ethylate reacts with benzamide bromide, although the number of products is different. The nitrophenyl urethane, $NO_2C_6H_4NHCOOC_2H_5$, the nitrophenylnitrobenzoyl urea, $NO_2C_6H_4NHCONHCOC_6H_4NO_2$, and the nitraniline, $NO_2C_6H_4NH_2$, are all products of the rearrangement of nitrobenzamide bromide $NO_2C_6H_4CONHBr$. From experiments 1 and 2 it is seen that in very dilute solution a very large amount (60–80 per cent.) of the amide bromide suffered rearrangement, so that in this fundamental manner sodium ethylate in ethyl alcohol acts just as sodium methylate in methyl alcohol,[1] or an aqueous solution of alkalies. The formation of free nitraniline in very dilute solutions is interesting, as it must be due to the saponification of the isocyanate, $NO_2C_6H_4NCO$, by the alkali, while in concentrated solution where there is less electrolytic dissociation such saponification does not seem to take place to any extent. Lengfeld and Stieglitz[2] observed the formation of paranitraniline in an analogous reaction where paranitrobenzamide bromide reacted with dilute sodium methylate in methyl alcohol. In this case in accordance with the stronger electrolytic dissociation of methyl alcohol solutions, the saponification occurs very prominently in a dilution of 1 : 100. The addition of a little water (Ex. 5) to a solution of sodium ethylate, 1 : 60, has the same effect. On increasing the electrolytic dissociation by this means the more concentrated solution gives considerable nitraniline.

V. *The Action of Sodium Ethylate on Succinimide Bromide:*

1. To 40 grams of absolute alcohol 1 gram of sodium was added, and to the cooled solution 8 grams (1 mol.) of well dried succinimide bromide. The sodium became slightly warm and the color changed to reddish brown. Heated twenty minutes on the water-bath the reaction was complete. On neutralizing the slightly alkaline solution with dilute acetic acid, and distilling off the alcohol, there remained a

[1] Lengfeld and Stieglitz: This JOURNAL, **15**, 215. [2] This JOURNAL, **16**, 370.

dark brown mass. This was extracted several times with chloroform. On cooling the solution, crystals were obtained which melted at 125° and were identified as succinimide. On concentrating the mother-liquor and adding ligroïn, at first more succinimide was precipitated. This was filtered off. An addition of more ligroïn now precipitated a silver-white, flaky, crystalline body, resembling very strongly in general appearance acetanilide. This recrystallized from ligroïn (boiling-point 30°–40°), melted at 78°. There was obtained less than 5 per cent., nor was the yield increased by repetition of the experiment.

2. On varying the conditions of the experiment the concentration was increased to 1.5 grams of sodium in 40 grams of absolute alcohol, and the molecular quantity of succinimide bromide, on cooling the solution. After the more energetic action had ceased the flask, closed with a calcium chloride tube, stood until succinimide bromide was no longer present in the solution. This took three days. The strongly alkaline solution was acidified with dilute acetic acid, which caused carbon dioxide to escape. Treating the contents of the flask as in experiment 1, there resulted almost 5 per cent. of the substance melting at 78°, and 60 per cent. of succinimide.

3. One gram of sodium was added to 40 grams of absolute alcohol and the solution was warmed to 45° when the molecular quantity of succinimide bromide was added in small portions. The action was very energetic, and at the end of ten minutes all the imide bromide had disappeared. The solution was slightly alkaline and when acidified with acetic acid gave off no carbon dioxide. Concentrating and extracting as before about 60 per cent. of succinimide was obtained, together with considerable tar, and less than 3 per cent. of the substance melting at 78°.

Several other conditions of temperature and of dilution of alcoholic solution did not essentially effect the yield. In general there resulted, of succinimide, 50–80 per cent.; of the substance melting at 78°, 3–5 per cent.; of tar, 10–30 per cent.

Analysis of the substance melting at 78° showed it to have the composition represented by the formula $C_8H_{15}NO_3$.

I. 0.2098 gram substance gave 18.2 cc. nitrogen at 18° and 746 mm.

II. 0.1827 gram substance gave 16.3 cc. nitrogen at 25° and 743 mm.

III. 0.1642 gram substance gave 0.2970 gram CO_2 and 0.1087 gram H_2O.

IV. 0.2293 gram substance gave 0.4196 grams CO_2 and 0.1571 gram H_2O.

	Calculated for $C_8H_{15}N_3N_3$.	Found. I.	II.	III.	IV.
Nitrogen	9.72	9.83	9.75	....	....
Carbon	50.00	....	....	49.88	49.88
Hydrogen	6.94	....	....	7.45	7.35

The method of formation and analysis indicate that this is identical in structure with the dimethyl succinylo-β-ureidopropionate obtained by Lengfeld and Stieglitz,[1] who determined its constitution and molecular weight.

The course of the reaction may be represented by the following equations:

$$1.\quad \begin{matrix}CH_2CO\\ |\\ CH_2CO\end{matrix}\!>\!NBr + NaOC_2H_5 = \begin{matrix}CH_2NCO\\ |\\ CH_2CO_2C_2H_5\end{matrix} + HOC_2H_5 + NaBr.$$

$$2.\quad \begin{matrix}CH_2CO\\ |\\ CH_2CO\end{matrix}\!>\!NBr + NaOC_2H_5 = \begin{matrix}CH_2CONH_2\\ |\\ CH_2CO_2C_2H_5\end{matrix} + CH_3CHO + NaBr.$$

$$3.\quad \begin{matrix}CH_2CONH_2\\ |\\ CH_2CO_2C_2H_5\end{matrix} + \begin{matrix}CH_2NCO\\ |\\ CH_2CO_2C_2H_5\end{matrix} = \begin{matrix}CH_2NHCONHCOCH_2\\ |\qquad\qquad\quad |\\ CH_2CO_2C_2H_5\qquad CH_2COC_2H_5\end{matrix}.$$

Diethyl succinylo-β-ureidopropionate is a silver-white substance resembling in appearance acetanilide. It is readily soluble in ether, acetone, alcohol, benzene, and chloroform. It is quite soluble in low-boiling ligroïn, from which it may be crystallized by cooling and prolonged stirring.

[1] This JOURNAL, **15**, 219.

The formation of the ethyl ester of carboethoxy-β-ureido-propionic acid, corresponding to the methyl ester obtained by Lengfeld and Stieglitz,[1] could not be accomplished.

The action of sodium ethylate in a solution of ethyl alcohol upon amide and amide bromides is twofold. It acts first as a reducing-agent regenerating the acid amide; secondly, as a rearranging-agent changing the amido bromide to a brom-formamide or isocyanate. The isocyanate may then react, first, with the alcohol present forming a urethane; second, with the acid amide generated by reduction of the amide bromide forming a symmetrical substituted urea; or, third, it may be saponified, forming the amine. The reaction is perfectly analogous to that of methyl alcoholate in a solution of methyl alcohol or of sodium hydroxide in aqueous solution on acid amide bromides. The products of the chemical change depend upon the concentration of the solution and the kind of amide bromides employed. In very concentrated solutions sodium ethylate acts almost wholly as a reducing-agent regenerating the acid amides. In more dilute solutions rearrangement is effected and urethanes or ureas result. In very dilute solutions where the ionization is greater, the isocyanate is saponified and amines are formed.

As a method of forming urethanes the yield is much smaller than when sodium methylate is employed in a solution of methyl alcohol.

Lengfeld and Stieglitz have ascertained that chlorformanilide and phenyl isocyanate are especially easily obtained from phenyl urethane by the action of phosphorus pentachloride and, since little study has been given to the aromatic isocyanates and few of them have been prepared, the nitrophenyl urethanes obtained in the previous experiments were used to test the general applicability of Lengfeld and Stieglitz's reaction, and to study such chlorformamides and isocyanates.

1. *Chloroform-o-Nitranilide.*—Since the methyl ester of orthonitrocarbamic acid is produced almost quantitatively by the action of sodium methylate in a solution of methyl alcohol it was used instead of the ethyl ester.

In a well dried flask phosphorus pentachloride (7.2 grams)

[1] This JOURNAL, 15, 215.

which had been previously washed with sodium-dried ligroïn (boiling-point 30°–40°), and the molecular quantity of methyl-orthonitrophenylurethane, and the two substances were carefully mixed by shaking. No reaction occurred at the ordinary temperature. The flask connected with a long delivery tube, which had been drawn out to a fine point, was heated on the water-bath. At 53° the urethane melted, but no chemical change was manifest. At 59° a few bubbles of gas appeared which became more numerous as the temperature was raised. At 70° the evolution of gas was quite rapid and this temperature was maintained for two hours where no more gas was formed. The escaping gas was identified as methyl chloride burning with a green-tinged flame as it escaped from the tube. On weighing the flask it was found to have decreased in weight 2.2 grams. The theoretical loss of weight for methyl chloride, CH_3Cl, was 1.86 grams. The slight excess may be accounted for by the volatility of the phosphorus oxychloride formed.

The flask now contained a slightly yellow liquid which, extracted with sodium-dried ligroïn, gave, when cooled in a freezing-mixture, white needle-shaped crystals, which, on recrystallizing from the same solvent, melted at 47°. The yield was about 70 per cent. of the theoretical for chloroformanilide, according to the equation

$$NO_2C_6H_4NHCO_2CH_3 + PCl_5 = NO_2C_6H_4NHCOCl + POCl_3 + CH_3Cl.$$

Crystals precipitated from ligroïn (boiling-point 20°–30°) and carefully pressed between filter paper, then allowed to stand twenty minutes in a vacuum-desiccator over vaseline and calcium chloride, gave the following results on analysis:

0.1612 gram heated with lime and precipitated with silver nitrate gave 0.1104 gram AgCl.

	Calculated for $C_7H_5N_2O_3Cl$.	Found.
Chlorine	17.44	16.89

The substance is very difficult to obtain pure for analysis, as it rapidly loses hydrochloric acid. When crystallized from ligroïn and dried over vaseline and calcium chloride in a

vacuum-desiccator for twelve hours analysis showed a loss of 18 per cent. of the chlorine contained.

0.2172 gram, analyzed as above, gave 0.1246 gram AgCl.

	Calculated for $C_7H_5N_2O_3Cl$.	Found.
Chlorine	17.44	14.19

The substance is readily soluble in chloroform, benzene, and ligroïn. In water it colors the solution yellow, forming nitraniline (melting-point 71°–72°):

(1) $NO_2C_6H_4NHCOCl + H_2O = NO_2C_6H_4NHCOOH + HCl$.

(2) $NO_2C_6H_4NHCOOH = CO_2 + NO_2C_6H_4NH_2$.

With methyl alcohol it forms yellow crystals which melt at 53°, and are identical with the methylorthonitrophenylurethane used as starting material. With ethyl alcohol it forms orthonitrophenylurethane melting at 58°. On standing it loses hydrochloric acid, and on long standing it changes to a white crystalline compound, which melts at 220°, insoluble or nearly so in all organic solvents.

Orthonitrophenylurethane.—The general method of preparing this was devised by Mr. O. K. Folin,[1] as a modification of the method of Lengfeld and Stieglitz for the preparation of metanitrophenyl isocyanate.

4.45 grams of phosphorus pentachloride, washed with sodium-dried ligroïn and the molecular quantity of methylorthonitrophenylurethane were heated in a flask for three hours, when no more gas was given off. The loss of weight of the flask was 1.18 grams. The calculated loss of weight in forming the chlorformanilide is 1.13 grams.

The phosphorus oxychloride was then distilled off in a current of dry hydrochloric acid. At the end of three hours the contents of the flask showed no further loss of weight. The loss was 3 grams; calculated loss for phosphorus oxychloride, 3.3 grams. A light-brown liquid remained which was heated in a slow current of dry air at 78°–80° and then for two hours at 90°, when hydrochloric acid ceased to be given off. There now remained in the flask 3.55 grams of material. The theoretical weight of the isocyanate to be formed was 3.27 grams. On extracting with ligroïn almost

[1] See note, p. 296.

all went into solution, a small quantity of tar remaining. On cooling the solution an almost white precipitate appeared which, on recrystallization, melted at 41°. The method of formation, analysis, and synthetic products showed the substance to be orthonitrophenyl isocyanate.

I. 0.1616 gram gave 24.3 cc. nitrogen at 15° and 741 mm.

II. 0.3393 gram gave 0.6377 gram CO_2 and 0.0801 gram H_2O.

	Calculated for $C_7H_4N_2O_3$.	Found. I.	Found. II.
Nitrogen	17.04	17.23	....
Carbon	51.27	....	51.08
Hydrogen	2.44	....	2.61

Orthonitrophenyl isocyanate, *o*-$NO_2C_6H_4NCO$, is an almost white solid melting at 41°. It crystallizes readily from low-boiling ligroïn in clusters of delicate needle-shaped crystals. It dissolves readily in chloroform, ether, and benzene. On standing in the air it turns yellow. With water it forms nitraniline. With ethyl and methyl alcohol it gives the corresponding urethanes. On standing twenty days in a vacuum 5 grams changed almost completely into a substance identical with that formed by long standing of chloroformnitranilide, which is probably the polymeric product, a cyanurate.

A number of derivatives of the isocyanate was prepared.

Isopropyl o-Nitrophenylcarbamate, *o*-$NO_2C_6H_4NHCO_2C_3H_7$.—To 1 gram of isopropyl alcohol 0.5 gram *o*-nitrophenyl isocyanate was added. The reaction began immediately with evolution of heat. The solution became yellow but no precipitate appeared. On driving off the excess of alcohol there remained a yellow oil, which crystallized after prolonged stirring in a freezing-mixture, but became an oil again at the temperature of the room. The oil dissolved in ligroïn, and, on cooling and stirring, crystallized in yellow cubes, which melted at 12°.

0.1606 gram gave 17.8 cc. nitrogen at 19° and 741 mm.

	Calculated for $C_{10}H_{12}N_2O_4$.	Found.
Nitrogen	12.5	12.47

Isobutyl o-Nitrophenylcarbamate, *o*-$NO_2C_6H_4NHCO_2C_4H_9$.—

When isobutyl alcohol was treated with *o*-nitrophenyl isocyanate in ethereal solution, it yielded yellow crystals, which melted at 13° and were soluble in alcohol and ether, but less soluble in low-boiling ligroïn than the corresponding ethyl urethane.

0.1624 gram gave 17.8 cc. nitrogen at 26° and 7.45 mm.

	Calculated for $C_{11}H_{14}N_2O_4$.	Found.
Nitrogen	11.76	11.86

Normal Amyl o-Nitrophenylcarbamate, $NO_2C_6H_4NHCO_2C_6H_{11}$. —This substance was prepared by adding orthonitrophenyl isocyanate to an excess of normal amyl alcohol, and driving off the excess of alcohol by heating on an oil-bath at 137°. The yellow oil which remained crystallized at —20° and, when precipitated from ligroïn, melted at —5°.

0.1960 gram gave 19.8 cc. nitrogen at 21° and 742 mm.

	Calculated for $C_{12}H_{16}N_2O_4$.	Found.
Nitrogen	11.1	11.26

Glycol Nitropheylmonocarbamate, *o*-$NO_2C_6H_4NHCO_2C_2H_4OH$. —To 1 gram of orthonitrophenyl isocyanate in ethereal solution glycol was added in slight excess of the ratio of 1 molecule of glycol to one of the isocyanate. Repeated shaking during two hours was required to get all the glycol into solution. When the ether was distilled off there remained a yellow oil which, by repeated crystallization from ligroïn (boiling-point 20°–30°), yielded a yellow crystalline body which analyses showed to be glycol orthonitrophenylmonocarbamate.

0.1932 gram gave 21.6 cc. nitrogen at 22° and 749 mm.

	Calculated for $C_9H_{10}N_2O_5$.	Found.
Nitrogen	12.39	12.54

Glycol orthonitrophenylmonocarbamate is a yellow crystalline substance which melts at 71° without decomposition. It dissolves readily in ether, alcohol, chloroform, and benzene, but with difficulty in ligroïn and water. It is not affected by alkalies or dilute acids in the cold, but when heated they readily decompose it. Its formation is expressed by the equation:

$$NO_2C_6H_4NCO + NOCH_2CH_2OH = NO_2C_6H_4NHCO_2CH_2CH_2OH.$$

Glycol o-Nitrophenyldicarbamate, $\begin{matrix} NO_2C_6N_4NHCO_2CH_2 \\ | \\ NO_2C_6H_4NHCO_2CH_2 \end{matrix}$.—To an ethereal solution of 1 gram of *o*-nitrophenyl isocyanate (2 mols.), 1 molecule of glycol was added, and the solution shaken till the glycol dissolved. When the ether was distilled off the yellow oil which remained was heated on the water-bath for twenty minutes to insure complete reaction. Cooled it readily crystallized. Purified by precipitating from ether by ligroïn the melting-point remained constant at 160°. The yield is quantitative. Analysis showed the substance to be glycol orthonitrophenyldicarbamate:

$$2NO_2C_6H_4NCO + \begin{matrix} HOCH_2 \\ | \\ HOCH_2 \end{matrix} = \begin{matrix} NO_2C_6H_4NHCO_2CH_2 \\ | \\ NO_2C_6H_4NHCO_2CH_2. \end{matrix}$$

0.1335 gram gave 17.5 cc. nitrogen at 24° and 743 mm.

	Calculated for $C_{16}H_{14}N_4O_8$.	Found.
Nitrogen	14.36	14.44

The dicarbamate is a yellow crystalline body melting at 160°. It dissolves with difficulty in ligroïn, is quite insoluble in water, but is more soluble in alcohol and ether than the corresponding monocarbamate.

Monoörthonitrocarbanilide, o-$NO_2C_6H_4NHCONHC_6H_5$.—When the molecular quantity of aniline dissolved in a few cc. of ether was added to an ethereal solution of *o*-nitrophenyl isocyanate, a precipitate was immediately formed which recrystallized from hot alcohol, melted at 170°. The yield was quantitative.

I. 0.1682 gram gave 0.3737 gram CO_2 and 0.0660 gram H_2O.

II. 0.1848 gram gave 27.4 cc. nitrogen at 23° and 745 mm.

	Calculated for $C_{13}H_{11}N_3O_3$.	Found.
Nitrogen	16.37	16.46
Hydrogen	4.28	4.36
Carbon	60.70	60.65

Mono-*o*-nitrocarbanilide is an almost white crystalline substance nearly insoluble in ether, ligroïn and cold alcohol, but readily soluble in hot alcohol.

Orthonitrophenylurea, o-$NO_2C_6H_4NHCONH_2$.—An ethereal solution of one gram of *o*-nitrophenyl isocyanate was saturated with a slow current of dry ammonia. The precipitate which formed immediately was washed with a little ether and recrystallized from hot methyl alcohol when crystals which melted at 181° were obtained.

0.1379 gram gave 28.4 cc. nitrogen at 18° and 744 mm.

	Calculated for $C_7H_7N_3O_3$.	Found.
Nitrogen	23.21	23.37

Symmetrical Orthonitrophenylorthotoluylurea, $NO_2C_6H_4NHCONHC_6H_4CH_3$.—This was obtained by the action of orthotoluidine and *o*-nitrophenyl isocyanate in ethereal solution. Crystallized from alcohol it melts at 189°. In all its properties it closely resembles orthonitrocarbanilide.

0.1989 gram gave 28.6 cc. nitrogen at 26° and 745 mm.

	Calculated for $C_{14}H_{13}N_3O_3$.	Found.
Nitrogen	15.5	15.75

The Action of Dialkylated Amines on Orthonitrophenyl Isocyanates.

Dialkylated amines are added to *o*-nitrophenyl isocyanate thus:

$$R_2NH + NO_2C_6H_4NCO = \begin{matrix} NO_2C_6H_4NH \\ R_2N \end{matrix} > CO.$$

The character of the reaction is very different from that of the aromatic amines. While the latter form crystalline compounds, in the formation of which chemical action is very energetic; the former give oils and heating is necessary.

Dimethyl o-Nitrophenylurea, $(CH_3)_2NCONHC_6H_4NO_2$.—Dry dimethylamine was passed into an ethereal solution of *o*-nitrophenyl isocyanate to saturation, but a portion of the solution tested with aniline precipitated orthonitrocarbanilide, showing the presence of unchanged isocyanate. The solution was then warmed and dimethylamine passed into it till a test

with aniline gave no precipitate. After the ether was driven off a yellow oil remained which became viscous at —15° and did not crystallize at —30°. This became mobile oil again at 0°. Analysis showed it to be dimethyl-*o*-nitrophenylurea.

0.1140 gram gave 20.7 cc. nitrogen at 23° and 753 mm.

	Calculated for $C_9H_{11}N_3O_3$.	Found.
Nitrogen	20.10	20.38

Diethyl-o-nitrophenylurea, $(C_2H_5)_2NCONHC_6H_4NO_2$.—This was formed by warming an ethereal solution of *o*-nitrophenyl isocyanate and diethylamine. Treating as above described for the corresponding dimethyl compound an oil was obtained which analysis showed to be diethyl-*o*-nitrophenyl urea.

0.1565 gram substance gave 25.4 cc. nitrogen at 23° and 743 mm.

	Calculated for $C_{11}H_{15}N_3O_3$.	Found.
Nitrogen	17.72	17.96

Dipropylorthonitrophenylurea, $(C_3H_7)_2NCOC_6H_4NO_2$, was formed by adding the molecular equivalent of *o*-nitrophenyl isocyanate to an ethereal solution of dipropylamine, except that reaction took place without heating. There is no difference between this and the dimethyl or diethylamine addition-products. Treated in the same way as above the urea remained as an oil.

0.2000 gram gave 29.1 cc. nitrogen at 25° and 748 mm.

	Calculated for $C_{13}H_{19}N_3O_3$.	Found.
Nitrogen	16.23	16.37

Dibutyl-o-nitrophenylurea, $(C_4H_9)_2NCONHC_6H_4NO$.—With *o*-nitrophenyl isocyanate dibutylamine behaved in exactly the same way as dipropylamine, yielding on oil which was prepared as just described.

0.1766 gram gave 23.1 cc. nitrogen at 23° and 748 mm.

	Calculated for $C_{15}H_{23}N_3O_3$.	Found.
Nitrogen	14.43	14.52

Diamyl-o-nitrophenylurea, $(C_5H_{11})NCONHC_6H_4NO_2$, was obtained from diamylamine and *o*-nitrophenyl isocyanate. Treated as above described with dipropylamine, perfectly

analogous results were obtained. The resulting oil proved to be diamyl-*o*-nitrophenylurea.

0.2259 gram gave 27.4 cc. nitrogen at 25° and 746 mm.

	Calculated for $C_{17}H_{27}N_3O_3$.	Found.
Nitrogen	13.12	13.36

Chlorformparanitranilide, $NO_2C_6H_4NHCOCl$, was prepared by treating methylparanitrophenylurethane with phosphorus pentachloride in the same manner as the corresponding ortho-nitrophenylurethane. It yielded about 50 per cent. of the urea chloride.

0.2304 gram heated with lime gave 0.1622 gram AgCl.

	Calculated for $C_7H_4N_2O_3$.	Found.
Chlorine	17.46	17.12

Chlorform-p-nitranilide closely resembles chlorformorthonitranilide. It is almost white with a very penetrating odor, causing tears. With ethyl and methyl alcohol it gives the corresponding urethanes. With ammonia and aniline it gives ureas. Heated above 44° it loses hydrochloric acid slowly and begins to melt. At 75° it loses all its hydrochloric acid and becomes an isocyanate.

Paranitrophenyl Isocyanate, *p*-$NO_2C_6H_4NCO$.—10 grams of chlorform-*p*-nitranilide in a flask with a long delivery tube were heated for 4 hours in a current of dry air at 70°–75°. There remained in the flask a brown liquid partially soluble in ligroïn, which when cooled, deposited almost white needles in concentric clusters. After two crystallizations they melted at 44°. The substance is *p*-nitrophenyl isocyanate.

0.1902 gram gave 29.4 cc. nitrogen at 24° and 747 mm.

	Calculated for $C_7H_4N_2O_3$.	Found.
Nitrogen	17.07	17.12

Water decomposes it giving nitraniline, while amines and alcohols are added to it, forming ureas and urethanes. Standing for a long it polymerizes. Heating hastens polymerization.

Isopropyl-p-nitrophenylurethane, *p*-$NO_2C_6H_4NHCOC_3H_7$, is formed by adding isopropyl alcohol to the molecular quantity

of *p*-nitrophenyl isocyanate. The yield is quantitative. The substance corresponds closely in properties to the methyl and ethyl compounds. It melts at 78°.

0.2293 gram gave 26.1 cc. nitrogen at 24° and 750 mm.

	Calculated for $C_{10}H_{12}N_2O_4$.	Found.
Nitrogen	12.5	12.66

Isobutyl-p-nitrophenylurethane, $NO_2C_6H_4NHCOC_4H_9$, is formed by the direct union of isobutyl alcohol and *p*-nitrophenyl isocyanate. The yield is quantitative. The substance melts at 62° and has properties analogous to the corresponding propylurethane.

0.2225 gram gave 23.6 cc. nitrogen at 24° and 750 mm.

	Calculated for $C_{11}H_{14}N_2O_4$.	Found.
Nitrogen	11.76	11.80

Paranitrocarbanilide, $NO_2C_6H_4NHCONHC_6H_5$. — When aniline is added to an ethereal solution of paranitrophenyl isocyanate, a precipitate is formed immediately which melts at 209° and appears to be identical with the substance described by Goldschmidt[1] (melting-point 202°), and by Leuckhart[2] (melting-point 212°).

0.2071 gram gave 30.8 cc. nitrogen at 24° and 741 mm.

	Calculated for $C_{13}H_{11}N_3O_3$.	Found.
Nitrogen	16.34	16.34

In conclusion I desire to express my sincere thanks to Professor Felix Lengfeld for the valuable assistance which he has given me in this work.

THE HYDROLYSIS OF ACID AMIDES.

By Ira Remsen.

A number of years ago, with the assistance of advanced workers in this laboratory, I carried out a series of investigations on the oxidation of substitution-products of aromatic hydrocarbons, the results of which went to show that, when the oxidizing agent is chromic acid, an oxidizable residue, situated in the ortho position with reference to an atom or

[1] Ber. d. chem. Ges., **26**, 2571. [2] J. prakt. Chem. **41**, 322.

group that is not oxidizable, is almost completely protected from oxidation, while similar groups in the meta or para position are easily oxidized. Later, experiments were tried on the reduction of nitro compounds of different structure, but, although results of some value were thus obtained, these have not been published, as I have hoped that the method of making the measurements might be improved. Still later, my attention was drawn to the marked difference between benzoic sulphinide (saccharin) and parasulphaminebenzoic acid[1] towards boiling dilute acids. The former is easily converted into the corresponding acid ammonium salt, while the latter remains unchanged.

About a year ago I requested Mr. E. E. Reid, of this laboratory, to make some experiments on the relative ease with which the three nitrobenzamides are converted into their ammonium salts by dilute acids. Mr. Reid has since devoted himself with much skill and energy to this work, and the results reached are most interesting. A method has been devised by which it is possible to measure with a considerable degree of accuracy the rate of the hydrolysis. The experiments thus far completed have been carried out with hydrochloric acid of three concentrations and with sulphuric acid of three concentrations. The details of the experiments will be communicated later, and it will then be seen that the curves showing the rate of change are remarkably regular. A striking difference is shown in the action of the three nitrobenzamides. The following results obtained with half normal hydrochloric acid may serve as an example:

Time in hours.	Per cent. of *o*-amide changed.	Per cent. of *m*-amide changed.	Per cent. of *p*-amide changed.
$\frac{1}{2}$	....	21.1	24.4
1	....	42.8	48.2
$1\frac{1}{2}$	....	50.1	63.4
2	....	65.0	71.2
3	3.3	80.5	84.5
4	3.9	88.9	91.9
5	....	92.6	94.6
6	6.2	94.2	96.9
7	....	....	....
8	8.6	....	....

[1] See Remsen and Burton: This JOURNAL, II, 403.

The ortho amide is seen to resist the action of the hydrolysing agent to a very marked degree, so that it was difficult to measure the amount of the change if the heating was not continued for at least three hours. On the other hand, the meta and para amides yield readily, the para somewhat more so than the meta.

It seems highly probable that other aromatic acid amides that contain an atom or group in the ortho position to the group, $CONH_2$, will conduct themselves in a similar way. These phenomena are suggestive of those studied in this laboratory many years ago, to which reference has already been made. Apparently the single nitro group in the ortho position with reference to the carbamide group, $CONH_2$, *protects* this from the action of dilute acids, as the nitro group in the ortho position to methyl protects this from oxidation by chromic acid, as shown in my earlier experiments. There is also some analogy between these protection phenomena, and those recently studied by Victor Meyer and his students—an analogy which Meyer does not appear to have recognized.

The object of this note is to inform chemists that we are in possession of a method that makes measurements of the kind given above comparatively easy, and that we propose to apply the method to the study of as large a number of cases as possible, with the object of determining

(1) Whether the influence of ortho groups upon the hydrolysis of acid amides is always the same; and

(2) How various atoms and groups differ in their effect upon the rate of hydrolysis.

This work will require some time and it seems best to postpone the publication of the results until the investigation is completed.[1]

[1] The substance of this note was communicated by me to the National Academy of Sciences, at the New York meeting held November 18, 1896.

REVIEWS.

LEHRBUCH DER ALLGEMEINEN CHEMIE. VON DR. WILHELM OSTWALD, Professor an der Universität zu Leipzig. Zweiten Bandes, zweiter Teil. Verwandtschaftslehre. Zweite umgearbeitete Auflage. Leipzig: Wilhelm Engelmann.

The first volume of this great text-book on physical chemistry, dealing with *stoichiometry*, and the first part of the second volume, treating of *thermochemistry*, *electrochemistry* and *photochemistry*, have already received notice some three years ago in this Journal.[1] The first instalment of the second part of the second and last volume has just appeared. This part will deal entirely with the question of chemical affinity in its broadest sense. The first two hundred pages, which have just come to hand, are devoted to the history of the subject. The first chapter discusses the history of chemical theories; the second, the older methods employed for determining the relative affinities of substances, together with the discussion to which the results led. In the third chapter, the more recent developments in the study of chemical affinity up to 1886, are treated historically. In this connection, the Law of Mass Action of Guldberg and Waage, the Phase Laws of J. W. Gibbs, the Studies in Chemical Dynamics by van't Hoff, and the Electrochemical Theory of Arrhenius, are especially to be mentioned. The last chapter treats of the advances which have been made since 1886, the most prominent being the van't Hoff Theory of Solutions, the Arrhenius Theory of Free Ions, the Applications of the Gas Laws to Solutions, and the Arrhenius Theory of Isohydric Solutions.

The publishers promise that this division of the *Lehrbuch* will be issued in four or five numbers, and will be completed during the coming year. A knowledge of this fact must be welcomed by all who are interested in physical chemistry, and especially by those who are called upon to teach that branch of science. For they will find here the subject of *affinity* treated in a complete and thoroughly systematic manner.

H. C. J.

[1] This JOURNAL, **15**, 533.